# Copper(I)–Terpyridine, an Efficient Catalyst for the Synthesis of Symmetrical Diaryl Trithiocarbonates

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**Abstract:** Symmetrical diaryl trithiocarbonates were readily synthesized in excellent yields by reaction of carbon disulfide and various aryl halides under mild reaction conditions in the presence of Copper(I) – Terpyridine as an efficient catalyst. This method allows the synthesis of symmetrical diaryl trithiocarbonates in short times without the use of highly toxic starting materials.

**Key words:** Symmetrical diaryl trithiocarbonates; copper iodide; terpyridine; carbon disulfide; aryl halides

The impact of organosulfur chemistry on modern organic synthesis is indisputable and has played an enormous role in biology, medicine and industry.[1] Among them, Organic trithiocarbonates constitute an important class of compounds which have been claimed for various applications in industry, synthesis and medicine.[2] They have been widely used as pesticides in agriculture,[3] lubricating additives,[4] in material science,[5] in froth flotation[6] for the recovery of minerals from their ores and for their absorption properties of the metals,[7] intermediates in organic synthesis,[8] for protection of thiol functionality,[9] in free radical polymerization reactions.[10] Additionally, they are used in various C–C bond forming reactions[11] which necessitates their preparation through convenient and safe methods.

The synthesis of trithiocarbonates has received considerable attention and several methods have been developed including reactions of thiols with thiophosgene,[12] chlorodithioformates,[13] or with carbon disulfide and alkyl halides under basic conditions in two-steps.[14] Other general method involves the dialkylation of the trithiocarbonate anion with halides, using phase-transfer catalysts or at elevated temperature.[15] However, each of the above methods has at least one of the following drawbacks: long reaction times, tedious work-up, low yields of product, synthetic inconvenient, employment of highly toxic chemicals with unpleasant odors, unavailability of starting materials, use of 10- to 19- fold molar excess amount of carbon disulfide and bases toward alkyl halides and formation of unwanted side products such as sulfides, etc. Consequently, developing new and convenient methods for the synthesis of symmetrical trithiocarbonates under mild reaction conditions is very valuable.

In recent years, transition-metal catalysis has intensely changed the face of modern organic chemistry by introducing a variety of novel synthetic methods. Transition metal catalysis of carbon-heteroatom bond formation are of great demand in general organic synthesis as well as the pharmaceutical industry and material science application.[16] Among them C(aryl)–S bond formation by the direct coupling of arylhalides and thiols or an in situ generated thiolate moiety[17] has received wide attention.[18] In the other hand, the tridentate 2,2':6',2''-terpyridines (tpys) have been of great interest over the last few years, mostly because of their ability to chelate transition metals.[19] Herein, according our previous study,[20] we report an efficient catalytic system for the synthesis of Symmetrical Diaryl Trithiocarbonates by using CuI and 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine (Mtpy) under mild reaction conditions.

To optimize the reaction with respect to catalyst, molar ratios of the catalyst aqnd ligang, base, and temperature we initially examined the reaction of iodobenzene and carbon disulfide as a model reaction, at various conditions under an aerobic atmosphere (Table 1).

As expected, the model reaction did not occur in the absence of catalyst (Table 1, entry 6) while only a 54% yield was obtained after 4 h in the absence of the ligand (Table 1, entry 13). Among the screened copper salts, copper(I) iodide resulted in the best performance (Table 1, entries 1, 7-10). Among the tested organic and inorganic bases, $CsOH.H_2O$ was found to be the most suitable base (Table 1, entries 1-5). Then, different copper iodide (0.5, 1 and 2 mol%) and ligand (0.5 and 1 mol%) concentrations were investigated (Table 1, entries 1, 11, 12 and 14); among them, 1 mol% of each were found to be the best (Table 1, entry 1).

After optimization, a variety of other ArX were shown to undergo the reaction smoothly, giving the desired products in high to excellent yields (Table 2).

When carbon disulfide (1 mmol) was added to the solution of $CsOH.H_2O$ (1 mmol) in DMSO (1 ml), and the mixture was stirred vigorously, the colorless mixture turned blood red immediately, indicating the formation of trithiocarbonate anion ($CS_3^{2-}$); in situ arylation with ArX for the appropriate times (Table 2) afforded the corresponding symmetrical trithiocarbonates in the presence of copper(I)–Mtpy as a catalyst. With progress of the reaction, the color of the solution changed from blood red to yellow. The structures of all the known products were established from their analytical and spectral (IR, $^1H$, and $^{13}C$ NMR) properties. Reactions of various aryl iodides such as iodobenzene, 4-iodoanisole, 2-iodotoluene, 2-iodoanisole, 4-iodobenzonitrile, and 1-iodonaphthalene were studied under the above optimized conditions (Table 2). The reactions proceeded well, and the corresponding diaryl trithiocarbonates were obtained in high yields. 2-Iodothiophene as a heterocyclic aryl iodide was found to react successfully, and the desire trithiocarbonate was produced in 93% yield (Table 2, entry 14).

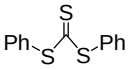
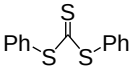
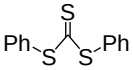
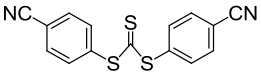
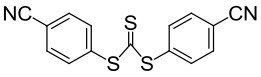
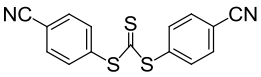
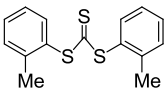
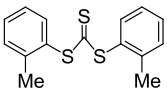
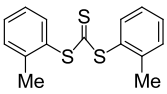
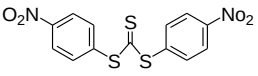
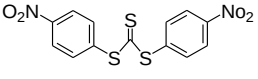
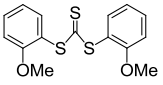
Table 1. Screening of the reaction conditions [a]

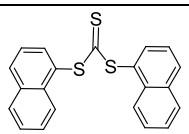
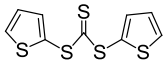
| Entry | Base | Catalyst (mol%) | Mtpy (mol%) | Time | Temp.(°C) | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | $CsOH.H_2O$ | CuI (1) | 1 | 90 min | 70 | 92 |
| 2 | $K_3PO_4$ | CuI (1) | 1 | 12 h | 100 | 70 |
| 3 | KOH | CuI (1) | 1 | 12 h | 100 | 53 |
| 4 | $Cs_2CO_3$ | CuI (1) | 1 | 24 h | 100 | 42 |
| 5 | $Et_3N$ | CuI (1) | 1 | 24 h | 100 | 12 |
| 6 | $CsOH.H_2O$ | - | - | 24 h | 110 | N.R. |
| 7 | $CsOH.H_2O$ | CuBr(1) | 1 | 90 min | 100 | 42 |
| 8 | $CsOH.H_2O$ | CuCl(1) | 1 | 90 min | 100 | 40 |
| 9 | $CsOH.H_2O$ | $Cu_2O$(1) | 1 | 90 min | 100 | 37 |
| 10 | $CsOH.H_2O$ | CuOAc(1) | 1 | 90 min | 100 | 32 |
| 11 | $CsOH.H_2O$ | CuI (0.5) | 1 | 90 min | 70 | 60 |
| 12 | $CsOH.H_2O$ | CuI (2) | 1 | 90 min | 70 | 90 |
| 13 | $CsOH.H_2O$ | CuI (1) | - | 4 h | 70 | 54 |
| 14 | $CsOH.H_2O$ | CuI (1) | 0.5 | 90 min | 70 | 74 |

[a] Reaction conditions: carbon disulfide (1 mmol), phenyl iodide (1 mmol), base (1 mmol), DMSO (1 ml).[b] Isolated yields.

Also, bromobenzene, 4-bromocyanobenzene and 2-bromotoluene as active bromoaryl substrates gave the desired trithiocarbonates in 65, 70 and 52% yield, respectively (Table 2, entries 2, 5 and 8). As expected, chlorobenzene reacted slowly under reaction conditions to give corresponding tritiocarbonate in the low yield (Table 2, entrie 3). Phenolic derivatives such as 4-cyano phenyl tosylate, o-tolyl tosylate were also found to react smoothly to afford the corresponding products in 91–84% yield (Table 2, entries 6 and 9).

Table 2. Synthesis of symmetrical diaryl trithiocarbonates

| Entry | Time | Temp. (°C) | product | Yield (%) [a, b] |
|---|---|---|---|---|
| 1 | 90 min | 70 |  | 92[18c] |
| 2 | 12 h | 100 |  | 65[18c] |
| 3 | 24 h | 100 |  | 41[18c] |
| 4 | 90 min | 70 |  | 94[18c] |
| 5 | 12 h | 100 |  | 70[18c] |
| 6 | 2 h | 70 |  | 91[18c] |
| 7 | 2 h | 70 |  | 86[18c] |
| 8 | 12 h | 100 |  | 52[18c] |
| 9 | 3 h | 70 |  | 84[18c] |
| 10 | 90 min | 70 |  | 95[18c] |
| 11 | 90 min | 70 |  | 94[18c] |
| 12 | 90 min | 70 |  | 90[18c] |

| | | | | |
|---|---|---|---|---|
| 13 | 90 min | 70 |  | 92[18c] |
| 14 | 90 min | 70 |  | 93[18c] |

[a] Isolated yields. [b] References are provided for known compounds.

In conclusion, copper(I)–terpyridine has been introduced as a potential catalyst for the synthesis of symmetrical diaryl trithiocarbonates. The specific advantages of this methodology include: mild reaction conditions, simple reaction work-up, short reaction times and high to excellent yield of the products without using large excess amount of toxic carbon disulfide.

**Procedures**

All chemicals were purchased from Merck. All products were identified by comparison of their spectral and physical data with those of the known samples.

IR spectra were obtained using an ABB FTLA 2000 instrument. $^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker DRX-400 Avance instrument with $CDCl_3$ as solution and the chemical shifts are determined by reference to residual $CHCl_3$ in $CDCl_3$. All compounds were characterized by comparing their physical data with those in the literature.

*General procedure for preparation of symmetrical diaryl trithiocarbonates:* To the blood red solution of $CsOH.H_2O$ (167 mg, 1.0 mmol) ), ArX (1.0 mmol) and carbon disulfide (76 mg, 1.0 mmol) in DMSO(1 ml), CuI(1 mol%) and Mtpy(1 mol%) were added and the reaction mixture was stirred at that temperature until the reaction was completed (monitored by TLC). On completion of the reaction, the mixture was filtered and evaporated, EtOAc (25 ml) was added and washed with water (2 × 15 ml) and dried over anhydrous $MgSO_4$. The solution was concentrated to give the crude product, which was purified by preparative TLC (silica gel, eluent, *n*-hexane).

**Diphenyl Carbonotrithioate (Table 2, Entry 1-3):** Pale yellow oil; IR (KBr) υ($cm^{-1}$): 1024 (C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm):7.26-7.65 (m, 10 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 196.0, 141.2, 127.7, 127.3, 127.2.

**Bis(4-Cyanophenyl) Carbonotrithioate (Table 2, Entry 4-6):** Yellow solid; mp: 115-118 ºC; IR (KBr) υ($cm^{-1}$): 2358, 2230, 1023 (C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm):7.72 (d, J= 8, 4H), 7.81 (d, J= 7.6, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 196.9, 143.5, 132.9, 127.9, 118.4, 112.4.

**Di-o-tolyl Carbonotrithioate (Table 2, Entry 7-9):** Pale yellow oil; IR (KBr) υ($cm^{-1}$): 1047 (C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.47-7.37 (m, 6H), 7.31-7.27 (m, 2H), 2.44 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 196.5, 143.9, 137.7, 131.1, 130.8, 130.7, 126.7, 20.9.

**Bis(4-Nitrophenyl) Carbonotrithioate (Table 2, Entry 10):** Orange solid; mp: 142-145 ºC; IR (KBr) υ($cm^{-1}$): 1514, 1082 (C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 8.00 (d, J= 8.8, 4H) 7.32 (d, J= 8.8, 4H);$^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 195.5, 1406, 138.7, 125.5,124.1.

**Bis(4-Methoxyphenyl) Carbonotrithioate (Table 2, Entry 11):** Pale yellow solid; mp: 98-100 ºC. IR (KBr) υ($cm^{-1}$): 1026 (C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.49-7.53 (m, 4H), 6.97-7.01 (m, 4H), 3.87 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm):199.7, 158.7, 133.5, 127.7, 114.1, 55.3.

**Bis(2-Methoxyphenyl) Carbonotrithioate (Table 2, Entry 12):** Pale yellow solid; mp: 92-95 ºC; IR (KBr) υ($cm^{-1}$):1068(C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.53 (t, J= 6.9, 2H), 7.42 (d, J= 7.8, 2H), 7.01-7.08 (m, 4H), 3.80 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm):197.1, 162.5, 139.8, 132.1, 121.4, 119.9, 112.2, 57.1.

**Di(Naphthalen-1-yl) Carbonotrithioate (Table 2, Entry 13):** Pale yellow solid; mp: 153-155 ºC. IR (KBr) υ($cm^{-1}$): 1038(C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 8.25 (d, J= 8.2, 2H), 8.14 (d, J= 8.1, 2H), 7.99 (d, J= 7.7, 2H), 7.51-7.58 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 197.6, 138.1, 136.6, 135.4, 132.6, 129.6, 128.9,126.2, 125.3, 124.8, 123.9.

**Di(Thiophen-2-yl) Carbonotrithioate (Table 2, Entry 14):** yellow solid; mp: 96-100 ºC; IR (KBr) υ($cm^{-1}$): 1047(C=S); $^{1}$HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.69(d, J= 5.1, 2H), 7.31 (d, J= 6, 2H), 7.10-7.15(m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm): 197.1, 139.7, 134.2, 129.6, 126.3.

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