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# $K_3PO_4$-mediated one-pot synthesis of symmetrical trithiocarbonates

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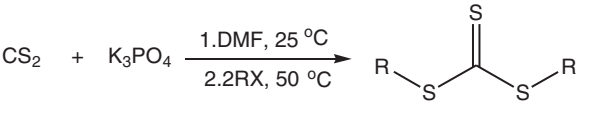
A new procedure has been developed for synthesis of symmetrical trithiocarbonates by one-pot reaction of carbon disulfide, and various alkyl halides in dimethylformamide using $K_3PO_4$ as an inexpensive and effective reagent.




**Keywords:** symmetrical trithiocarbonates; potassium phosphate; one-pot reaction; carbon disulfide; alkyl halides

## 1. Introduction

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, symmetrical and unsymmetrical trithiocarbonates represent an important class of key compounds that have been utilized as intermediates, pesticides and nematocides in agriculture (*2–4*), and as lubricating additives (*3*,*4* and references cited therein, *5*). In addition, radical polymerization with thiocarbonylthio reversible addition–fragmentation chain-transfer (RAFT) agents (*6–8*) is arguably one of the most versatile processes for free-radical living polymerization, displaying superior flexibility with respect to monomers and reaction conditions. For instance, dibenzyl trithiocarbonate derivatives are well established RAFT agents (*8*, *9*), which enables controlled free-radical polymerization of various vinyl monomers to afford polymers with narrow polydispersity and controlled molecular weights.

Several synthetic methods for the preparation of trithiocarbonates have been developed, including reactions of thiols with either thiophosgene (*10*) or chlorodithioformates (*4*), dialkylation of trithicarbonate anion ($CS_3^{2-}$) with alkyl halides (*11*), one-pot reactions involving carbon disulfide,

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sodium sulfide, alkyl halides, and alkyl thiols under phase-transfer catalytic conditions at 70°C (*3*), reaction of potassium carbonotrithioates with diaryliodonium salts in ionic liquids (*12*), reaction of alkyl halides with $CS_2$ in the presence of phase-transfer catalysts (*13*), and hydroxide form of anion exchange resin (amberlyst A-26) (*14*). However, most of the reported methods suffer from various disadvantages such as unavailability of starting materials, employment of highly toxic chemicals with unpleasant odors, the use of 10- to 19-fold molar excess amount of carbon disulfide and bases toward alkyl halides, synthetic inconvenience, and the formation of unwanted side products such as sulfides. Recently, Aoyagi *et al.* (*15*) reported a one-step synthesis of symmetrical trithiocarbonates by the equimolar reaction of alkyl halides with $CS_2$ and cesium carbonate under ambient conditions; but, this reagent is rather expensive. In the same year, Wood *et al.* (*16*) introduced a method for the synthesis of symmetrical trithiocarbonates using 1,1′-thiocarbonyl diimidazole and primary thiols; this method, however, needs an inert atmosphere and gives moderate yields of the product. In two separate reports, Chaturvedi *et al.* (*17*) described the synthesis of trithiocarbonates from thiols (*17*) and alcoholic tosylates (*17*), using the Mitsunobu reagent and $Cs_2CO_3/CS_2$ system, respectively. In a previous study (*18*), we investigated the one-pot synthesis of symmetrical dialkyl trithiocarbonates by the reaction of alkyl halides with $CS_2$ at room temperature in an aerobic atmosphere catalyzed by $KF/Al_2O_3$.

## 2. Results and discussion

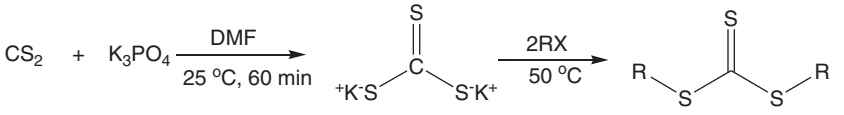
Tripotassium phosphate, $K_3PO_4$, continues to attract much attention from organic chemists due to the versatility of use in synthetic chemistry; it is cheap, non-toxic, and a strong inorganic base (pKa 12.32 for the conjugate acid), used as an alternative non-nucleophilic base in several reactions (*19*). We have now developed an easy and highly convenient methodology for one-pot synthesis of a variety of symmetrical dialkyl trithiocarbonates by the reaction of alkyl halides with $CS_2$ in an aerobic atmosphere mediated by anhydrous $K_3PO_4$ in dry dimethylformamide (DMF) at 50°C.

In order to optimize the reaction condition with respect to temperature, solvent, and molar ratios of the components, we initially conducted the reaction of benzyl bromide (1.0 mmol) and carbon disulfide (1.5 mmol), as a model reaction, at various conditions under an aerobic atmosphere (Table 1). The best result was obtained when 1.0 mmol of $K_3PO_4$ in DMF at 50°C was used (Entry 8, Table 1). No change of color to blood red was observed when other solvents such as THF, DMSO, 1,4-dioxane, $CH_2Cl_2$, acetone, and toluene were used at 25°C; this observation indicates that the trithiocarbonate anion ($CS_3^{2-}$) intermediate was not formed.

Table 1. Optimization of the $K_3PO_4$-mediated trithiocarbonation of benzyl bromide.

| Entry | Solvent | mmol of catalyst | Condition | Yield[a] (%) |
|---|---|---|---|---|
| 1 | THF | 1 | 25°C; 6 h | N.R. |
| 2 | DMSO | 1 | 25°C; 6 h | N.R. |
| 3 | 1,4-Dioxane | 1 | 25°C; 6 h | N.R. |
| 4 | $CH_2Cl_2$ | 1 | 25°C; 6 h | N.R. |
| 5 | Acetone | 1 | 25°C; 6 h | N.R. |
| 6 | Toluene | 1 | 25°C; 6 h | N.R. |
| 7 | DMF | 1 | 25°C; 14 h | 28 |
| 8 | DMF | 1 | 50°C; 10 h | 92 |
| 9 | DMF | 1 | 70°C; 6 h | 85 |
| 10 | DMF | 2 | 50°C; 10 h | 93 |
| 11 | DMF | 3 | 50°C; 10 h | 45 |
| 12 | DMF | 0.5 | 50°C; 10 h | N.R. |

Note: [a]Isolated yields.



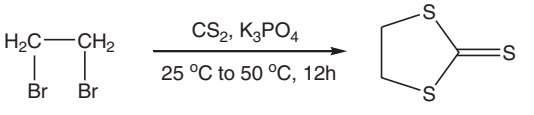

Scheme 1. Preparation of symmetrical trithiocarbonates.

Table 2. Synthesis of symmetrical trithiocarbonates mediated by $K_3PO_4$.

| Entry | Alkyl halide | Time (h) | Yield[a,b] (%) |
|---|---|---|---|
| 1 | $PhCH_2Br$ | 10 | 92 (*18*) |
| 2 | $CH_3I$ | 9 | 75 (*18*) |
| 3 | $CH_3CH_2I$ | 10 | 82 (*18*) |
| 4 | $CH_3(CH_2)_4CH_2Br$ | 12 | 90 (*18*) |
| 5 | $CH_3(CH_2)_6CH_2I$ | 12 | 89 (*18*) |
| 6 | $CH_2{=}CHCH_2Br$ | 11 | 79 (*18*) |
| 7 | $CH_2{=}CHCH_2Cl$ | 12 | 76 (*18*) |
| 8 | 4-$BrC_6H_4CH_2Br$ | 10 | 78 (*13b*) |
| 9 | $PhCH(CH_3)Br$ | 10 | 81 (*18*) |
| 10 | $PhC(CH_3)_2Br$ | 24 | N.R. |
| 11 | $BrCH_2CH_2Br$ | 12 | 71 (*13*) |
| 12 | $CH_3CH_2CH(CH_3)Br$ | 20 | 72 (*18*) |
| 13 | $(CH_3)_2CHBr$ | 8 | 78 (*18*) |
| 14 | $(CH_3)_3CBr$ | 24 | N.R. |

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

After optimization, a variety of other alkyl halides were shown to undergo the reaction smoothly, giving the desired products in high to excellent yields (Scheme 1). The results are summarized in Table 2.




Scheme 2. Formation of 1,3-dithiolane-2-thione.

The blood red trithiocarbonate anion ($CS_3^{2-}$) is known to be formed by reacting ammonium sulfide, strong aqueous ammonia or alkali metal sulfides with carbon disulfide (*20*). When carbon disulfide (1.5 mmol) was added to the suspension of anhydrous $K_3PO_4$ (1.0 mmol) in dry DMF (2 ml), and the mixture was stirred vigorously at 25°C, the colorless mixture turned blood red within 60 min, indicating the formation of trithiocarbonate anion (*20*). *In situ* alkylation with alkyl halides for the appropriate times (Table 2) afforded the corresponding symmetrical trithiocarbonates. With the progress of the reaction, the color of the solution changed from blood red to yellow. The structures of all the products were established from their analytical and spectral (IR, $^1H$, and $^{13}C$ NMR) properties. Primary, secondary, benzylic, and allylic halides are converted to the corresponding trithiocarbonates as exclusive and virtually pure products according to TLC and $^1H$ NMR, in high yields (Table 2).

The procedure worked fine with primary, secondary, benzyl as well as allyl halides. Under the same reaction conditions, tertiary halides (Entries 10 and 14, Table 2) did not produce the expected trithiocarbonates even after 24 h. In addition, cyclic trithiocarbonate such as 1,3-dithiolane-2-thione can also be prepared from 1,2-dibromoethane (Entry 11, Table 2) without the formation of any polymeric by-product (Scheme 2). The result clearly shows that $K_3PO_4$ is an efficient reagent in trithiocarbonation of alkyl halides.

## 3. Conclusion

In conclusion, the $K_3PO_4$-mediated procedure reported here for the synthesis of a wide variety of symmetrical trithiocarbonates offers some notable and distinct advantages over procedures usually employed, such as operational simplicity, mild reaction conditions, simple reaction work-up, high yield of the products without using large excess amount of toxic carbon disulfide, and the use of a cheap basic reagent.



## 4. Experimental

All products were identified by comparison of their spectral and physical data with those of known samples. IR spectra were obtained using an ABB FTLA 2000 instrument. NMR spectra were recorded on a Bruker DRX-400 Avance instrument at 400 MHz for $^1$H and at 100 MHz for $^{13}$C in $CDCl_3$ solutions.

### 4.1. *General procedure*

Anhydrous $K_3PO_4$ (2.0 mmol) was added to a solution of carbon disulfide (3.0 mmol) in dry DMF (2 ml) and the mixture was stirred at 25°C for 60 min. The color of the mixture changed from light yellow to blood red; then, alkyl halide (2.0 mmol) was added to the above suspension, and the reaction mixture stirred at 50°C until the reaction was completed (monitored by TLC). On completion of the reaction, the mixture was filtered and evaporated, EtOAc (25 ml) was added, washed with water (2 × 15 ml), and dried over anhydrous $MgSO_4$. The solution was evaporated to give the crude trithiocarbonate, which was purified by preparative TLC (silica gel, eluent, *n*-hexane).

### 4.2. *Selected physical and spectral data*

#### 4.2.1. *Dibenzyl trithiocarbonate (Table 2, Entry 1)*

Light yellow oil; IR (neat): 1062 (C=S), 1494, 1602 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.67 (s, 4H), 7.28–7.40 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 41.59, 127.86, 128.77, 129.34, 134.96, 222.80.

#### 4.2.2. *Di-n-hexyl trithiocarbonate (Table 2, Entry 4)*

Yellow oil; IR (neat): 1057 (C=S) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.92 (t, $J$ = 6.8 Hz, 6H), 1.27–1.35 (m, 8H), 1.40–1.45 (m, 4H), 1.72 (quin, $J$ = 7.6 Hz, 4H), 3.39 (t, $J$ = 7.6 Hz, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.04, 22.53, 28.02, 28.64, 31.33, 36.88, 224.78.

#### 4.2.3. *Diallyl trithiocarbonate (Table 2, Entries 6 and 7)*

Light yellow oil; IR (neat): 1057 (C=S), 1638 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.07 (d, $J$ = 6.8 Hz, 4H), 5.23 (d, $J$ = 10.0 Hz, 2H), 5.36 (d, $J$ = 17.0, 1.3 Hz, 2H), 5.85–5.95 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 39.72, 119.72, 130.97, 222.48.

#### 4.2.4. *Bis(1-phenylethyl)carbonotrithioate (Table 2, Entry 9)*

Yellow oil; IR (neat): 1069 (C=S), 1449, 1493, 1596 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.82 (d, $J = 7.6$ Hz, 6H), 5.39 (q, $J = 7.6$ Hz, 2H), 7.35–7.41 (m, 10H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.41, 50.10, 127.77, 128.44, 128.71, 141.13, 221.44.

#### 4.2.5. *1,3-Dithiolane-2-thion (Table 2, Entry 11)*

Yellow oil; IR (neat): 1075 (C=S) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.99 (s, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 43.86, 228.68.

#### 4.2.6. *Diisopropyl trithiocarbonate (Table 2, Entry 13)*

Light yellow oil; IR (neat): 1073 (C=S) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.42 (d, $J = 7.2$ Hz, 12H), 4.22 (sept, $J = 7.2$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 22.07, 41.63, 223.48.

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## References

(1) Page, P.C.B. *Organo-Sulfur Chemistry I & II*; Springer: Berlin, 1999.
(2) (a) Renner, H.J.; Schneider, G.; Weissflog, J. Ger (East) **1954,** 15431; Renner, H.J.; Schneider, G.; Weissflog, *Chem. Abstr.* **1960,** *54,* 2650f; (b) Bashour, J.T. US Patent 2676129, 1954; Renner, H.J.; Schneider, G.; Weissflog, *Chem. Abstr.* **1954,** *48,* 8472i; US Patent 2731487, 1956; Renner, H.J.; Schneider, G.; Weissflog, *Chem. Abstr.* **1956,** *50,* 15583h.
(3) Degani, L.; Fochi, R.; Gatti, A.; Regondi, V. *Synthesis* **1986,** 894–899.
(4) Godt, H.C., Jr.; Wanns, A.E. *J. Org. Chem.* **1961,** *26,* 4047–4051.
(5) Blake, E.S. US Patent 2396487, 1946; Blake, E.S. *Chem. Abstr.* **1946,** *40,* 2974.
(6) Chiefari, J.; Chong, B.Y.K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.P.T; Mayadunne, R.T.A.; Meijs, G.F.; Moad, C.L.; Moad, G.; Rizzardo, E.; Thang, S.H. *Macromolecules* **1998,** *31,* 5559–5562.
(7) Barner-Kowollik, C.; Davis, T.P.; Heuts, J.P.A.; Stenzel, M.H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003,** *41,* 365–375.
(8) Chiefari, J.; Mayandunne, R.T.A.; Moad, C.L.; Moad, G.; Rizzardo, E.; Postma, A.; Thang, S.H. *Macromolecules* **2003,** *36,* 2273–2283.
(9) You, Y.-Z.; Hong, C.-Y.; Pan, C.-Y. *Chem. Commun.* **2002,** 2800–2801.
(10) Runge, F.; El-Hewehi, Z. *J. Prakt. Chem.* **1959,** *10,* 268–272.
(11) Runge, F.; El-Hewehi, Z.; Renner, H.J.; Taeger, E. *J. Prakt. Chem.* **1960,** *11,* 284–289.
(12) Wang, F.-Y.; Chen, Z.-C.; Zheng, Q.-G, *J. Chem. Res. (S)* **2003,** 810–811.
(13) (a) Lee, A.W.M.; Chan, W.H.; Wong, H.C. *Synth. Commun.* **1988,** *18,* 1531–1536; (b) Kiasat, A.R.; Mehrjardi, M.F. *J. Chin. Chem. Soc.* **2008,** *55,* 639–642.
(14) Tamami, B.; Kiasat, A.R. *Iran. Polym. J.* **1999,** *8,* 17–23.
(15) Aoyagi, N.; Ochiai, B.; Mori, H.; Endo, T. *Synlett* **2006,** 636–638.
(16) Wood, M.R.; Duncalf, D.J.; Rannard, S.P.; Perrier, S. *Org. Lett.* **2006,** *8,* 553–556.
(17) (a) Chaturvedi, D.; Chaturvedi, A.K.; Mishra, N.; Mishra, V. *Tetrahedron Lett.* **2008,** *49,* 4886–4888; (b) Chaturvedi, D.; Mishra, N.; Chaturvedi, A.K.; Mishra, V. *Monatsh. Chem.* **2008,** *139,* 1467–1470.
(18) Movassagh, B.; Soleiman-Beigi, M.; Nazari, M. *Chem. Lett.* **2008,** *37,* 22–23.
(19) (a) Shirakawa, E.; Kibata, T.; Otsuka, H.; Tsuchimoto, T. *Tetrahedron* **2005,** *61,* 9878–9885; (b) Beletskaya, I.P.; Cheprakov, A.V. *Chem. Rev.* **2000,** *100,* 3009–3066; (c) Yao, Q.; Kinney, E.P.; Yang, Z. *J. Org. Chem*. **2003,** *68,* 7528–7531; (d) Niu, J.; Zhou, H.; Li, Z.; Xu, J.; Hu, S. *J. Org. Chem*. **2008,** *73,* 7814–7817; (e) Niu, J.; Guo, P.; Kang, J.; Li, Z.; Xu, J.; Hu, S. *J. Org. Chem*. **2009,** *74,* 5075–5078; (f) Movassagh, B.; Khosousi, S. *Monatsh. Chem.* In press.
(20) Wertheim, E. *J. Am. Chem. Soc.* **1926,** *48,* 826–830.