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# Synthesis of *S*-Aryl/Alkyl Thiolcarbonates from Disulfides and Chloroformates in the Presence of the $Zn/AlCl_3$ System

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**Summary.** A simple, general, and high yielding method has been developed for the synthesis of *S*-aryl/alkyl-*O*-aryl/alkyl thiolcarbonates from various chloroformates and disulfides by reductive cleavage of the S–S bond with a $Zn/AlCl_3$ system in dry acetonitrile at 80°C.

**Keywords.** Thiolcarbonates; Disulfides; Chloroformates; Zinc thiolates.

## Introduction

Thiolcarbonates are an important class of compounds, being useful as synthesis intermediates in the preparation of other valuable substances [1, 2], polymerization inhibitors [3], heat stabilizers for polymers [4], precursors to polymercaptanes [5], bioactive compounds [6], radiographic contrast agent [7], and as biological toxicants, particularly as nematocides [8]. Of classical methods for the preparation of thiolcarbonates, we can cite those involving the reaction of primary and benzyl alcohols with carbon dioxide, methanesulfonic anhydride, and thiols under basic conditions [9], the rearrangement of diaryl thioncarbonates [*Ar*OC(S)O*Ar*] [10], the treatment of thiols with chloroformates [7], the reaction of aryloxide salts, carbonyl sulfide and alkyl halides [11], the reaction of trimethylsilyl enol ethers with phenyl thiofluoroformate in the presence of a naked fluoride ion catalyst [12], the reaction of $\beta$-nitroalcohols and 2,2,2-trihaloethanols with ethyl chlorothiolformate in the presence of anhydrous iron(III) chloride [13], nucleophilic addition of potassium monothiocarbonates to epoxides or alkyl halides [14], selenium catalyzed reaction of alcohols, carbon monoxide, sulfur, and alkyl halides [15], and sulfur-assisted *O*-carbonylation of alcohols with carbon monoxide in the presence of *DBU* [16]. Unfortunately, most of the reported methods suffer from serious drawbacks such as difficultly available reagents, low yields, the use of poisonous phosgene and carbonyl sulfide, the need of intolerable odorous thiols, the use of moisture sensitive chlorothioformate, preparation of certain thiolcarbonate derivatives, and multi-step procedures. Very recently, a new selenium-catalyzed reaction of alcohols with carbon monoxide and diaryl disulfides was introduced for synthesis of *S*-aryl-*O*-alkyl thiolcarbonates [17].

## Results and Discussion

As part of our ongoing work on the $Zn/AlCl_3$ system, we describe a useful and general method for the synthesis of various *S*-aryl/alkyl-*O*-aryl/alkyl thiolcarbonates **3** from disulfides **1** and chloroformates **2** by reductive cleavage of the S–S bond with a $Zn/AlCl_3$ system in dry acetonitrile at 80°C according to Scheme 1.

A series of symmetrical alkyl and aryl disulfides were treated with phenyl and benzyl chloroformates

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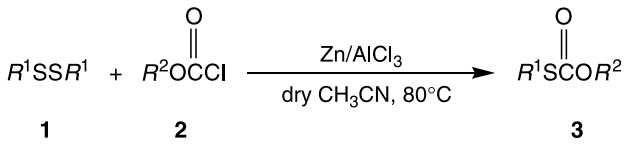


**Scheme 1**

**Table 1.** Synthesis of various thiolcarbonates **3** from disulfides **1** and chloroformates **2**

| Entry | $R^1$ | $R^2$ | Reaction time/min | Product | Isolated yield/% |
|---|---|---|---|---|---|
| 1 | *Ph* | *Ph* | 45 | **3a** | 90 [2g] |
| 2 | *Ph* | $PhCH_2$ | 60 | **3b** | 65 [20] |
| 3 | 4-*Br*$C_6H_4$ | *Ph* | 60 | **3c** | 88 |
| 4 | 4-Cl$C_6H_4$ | *Ph* | 60 | **3d** | 89 [10] |
| 5 | 4-Cl$C_6H_4$ | $PhCH_2$ | 90 | **3e** | 85 |
| 6 | 4-Me$C_6H_4$ | *Ph* | 45 | **3f** | 86 |
| 7 | 4-MeO$C_6H_4$ | *Ph* | 45 | **3g** | 86 |
| 8 | $PhCH_2$ | *Ph* | 60 | **3h** | 72 [19] |
| 9 | $PhCH_2$ | $PhCH_2$ | 90 | **3i** | 66 [19] |
| 10 | $CH_3$ | *Ph* | 60 | **3j** | 87 [11] |

in the presence of the $Zn/AlCl_3$ system with a molar ratio of disulfide:$AlCl_3$:chloroformate = 0.5:1:1.5. The disappearance of zinc powder during the preliminary treatment of disulfides with $Zn/AlCl_3$ is attributed to the formation of a zinc thiolate intermediate [18], which further undergoes nucleophilic attack to the chloroformate to afford the thiolcarbonates in high yields.

The results are summarized in Table 1. Reactions are very clean and thiolcarbonates are obtained as the sole product during short times. The work-up of the reaction is accomplished by simple filtration and evaporation of the organic solvent ($CH_3CN$) and final purification.

In conclusion, the present method introduces a simple, more general, and high yielding route to a wide variety of thiolcarbonate derivatives with shorter reaction times to the ones reported previously. Also, it offers some advantages over earlier reported procedures, in that it avoids the need to apply foul-smelling thiols, multi-step procedures, and the use of complex starting materials.

## Experimental

$^1H$ (300 MHz) and $^{13}C$ (75 MHz) NMR spectra were recorded using a Bruker AQS-300 Avance spectrometer. IR spectra were obtained using an ABB FTLA 2000 instrument. Mass spectra were recorded with a *Hewlett-Packard* model 5973 instrument. Melting points and boiling points were determined by a Büchi B-540 melting point/boiling point capillary apparatus.

*General Procedure for Synthesis of Thiolcarbonates from Disulfides and Chloroformates*

A mixture of 0.5 mmol disulfide, 130 mg Zn powder (2.0 mmol), 134 mg finely ground anhydrous $AlCl_3$ (1.0 mmol), and 6 $cm^3$ dry acetonitrile was stirred at 80°C for 1.5 h until the zinc powder had almost disappeared. The chloroformate (1.5 mmol) was then added at once to the solution and stirring was continued at that temperature for the appropriate time (Table 1). After completion of the reaction as indicated by TLC, the solution was filtered, acetonitrile was evaporated, 20 $cm^3$ $CHCl_3$ was added, the mixture washed with water ($2 \times 10$ $cm^3$), and the organic layer was dried ($Na_2SO_4$). The solvent was evaporated under reduced pressure, and the crude mixture was purified by preparative TLC (silica gel; eluent, *n*-heptane:EtO*Ac* = 6:1) to obtain the pure product. All products were characterized by infrared, $^1H$ and $^{13}C$ NMR spectroscopy, and finally by comparison with authentic samples.

*Phenyl S-(4-bromophenyl) thiocarbonate* (**3c**, $C_{13}H_9BrO_2S$) Mp 89–91°C; IR (KBr): $\bar{\nu} = 1735$ (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 7.20$ (dd, $J = 8.4$, 8.2 Hz, *Ph*), 7.27 (t, $J = 8.3$ Hz, *Ph*), 7.42 (d, $J = 8.4$ Hz, *Ph*) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 121.1$, 125.7, 126.3, 129.54, 129.56, 136.03, 136.37, 151.2, 168.3 ppm; EIMS: $m/z$ (%) = 310 $(M+2)^+$ (51), 308 ($M^+$, 49), 282 (81), 280 (78), 189 (73), 187 (72), 108 (100), 77 (53), 65 (44), 39 (47).

*Benzyl S-(4-chlorophenyl) thiocarbonate* (**3e**, $C_{14}H_{11}ClO_2S$) Mp 55–56°C; IR (KBr): $\bar{\nu} = 1730$ (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 4.10$ (s, $CH_2$), 7.26 (d, $J = 8.6$ Hz, *Ph*), 7.30 (d, $J = 8.6$ Hz, *Ph*) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 39.3$, 127.3, 128.54, 128.78, 128.94, 129.1, 131.4, 134.6, 137.1, 168.2 ppm; EIMS $m/z$ (%) = 280 $(M+2)^+$ (0.2), 278 ($M^+$, 0.6), 236 (19), 234 (51), 108 (14), 91 (100), 65 (33), 39 (14).

*Phenyl S-(4-methylphenyl) thiocarbonate* (**3f**, $C_{14}H_{12}O_2S$) Mp 84–86°C; IR (KBr): $\bar{\nu} = 1730$ (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 2.41$ (s, $CH_3$), 7.18–7.28 (m, *Ph*), 7.38 (t, $J = 8.1$ Hz, *Ph*), 7.49 (d, $J = 8.1$ Hz, *Ph*) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 21.4$, 121.2, 123.6, 126.1, 129.4, 130.1, 134.8, 140.3, 151.3, 169.1 ppm; EIMS $m/z$ (%) = 244 ($M^+$, 44), 216 (52), 151 (28), 123 (100), 77 (32), 65 (20), 39 (19).

*Phenyl S-(4-methoxyphenyl) thiocarbonate* (**3g**, $C_{14}H_{12}O_3S$) Mp 52–53°C; IR (KBr): $\bar{\nu} = 1735$ (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 3.84$ (s, $CH_3$), 6.98 (d, $J = 8.8$ Hz, *Ph*), 7.19–7.28 (m, *Ph*), 7.40 (t, $J = 7.8$ Hz, *Ph*), 7.55 (d, $J = 8.8$ Hz, *Ph*) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta = 55.4$, 114.9, 117.7, 121.2, 126.1, 129.5, 136.7, 151.4, 161.1, 169.5 ppm; EIMS $m/z$ (%) = 260 ($M^+$, 35), 232 (5), 139 (100), 124 (4), 95 (9), 77 (9), 65 (7), 39 (9).

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