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# NOVEL SYNTHESIS OF SYMMETRICAL DIALKYL/DIARYL-ALKYLTRITHIOCARBONATES IN NON-AQUEOUS MEDIUM AT ROOM TEMPERATURE USING $CS_2$, $CS_2CO_3$ AND ALKYL/ARYL-ALKYL HALIDES

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**ABSTRACT**

One step new method for the synthesizing symmetric Dialkyl/Diaryl-alkylTrithiocarbonates by a number of $1^0$, $2^0$ and $3^0$ alkyl/aryl-alkyl halides making use of $Cs_2CO_3$ in $CS_2$ and DMSO is being reported. This method of synthesis is more efficient, cheaper, greener compared to the other available methods.

**Keywords:**Dialkyl/Diaryl-alkyltrithiocarbonates, alkyl halides, aryl-alkyl halides, Carbon disulfide, Cesium carbonate, Dimethyl sulphoxide.



## INTRODUCTION

Dialkyl/Diaryl-alkyltrithiocarbonates are some very significant class of compounds which are used as agro-chemicals[1-3] and additives for lubricants[4-6]. The derivatives of dibenzyltrithiocarbonates (DBTTC) have been potentially used in reversible and addition fragmentation in chain transfer[7-11] reactions. Organic Trithiocarbonates are some major compounds due to their extensive use in synthetic chemistry, industrial processes and medicinal field[12-15].Thus, a cheaper, easier and eco-friendly synthesis of trithiocarbonates is always desired. Classical production of Trithiocarbonates made the use of reactions between thiols and thiophosgene[16] or chlorodithioformates[17].Another method involved reactions between thiols, $CS_2$ and R-X (R= alkyl, aryl-alkyl group) under alkaline conditions[18].

Such synthesis, however, used toxic reagents with obnoxious odor. Another general method to synthesizetrithiocarbonates is by alkylation of thrithiocarbonate[19]anion by alkyl halides using phase transfer catalysis or reacting them at higher temperatures (70°C). The dialkylation and diarylation are also not very convenient, as it needs a very high amount of $CS_2$ and bases to react with alkyl/aryl-alkyl halides. Due to the toxic nature and unpleasant odor of $CS_2$, a process is needed which require the least possible quantity of carbon disulfide for much effective and sustaining production of trithiocarbonates. So, we go on to discover new and improved methods.

Our research colleagues and various other renowned scientists are engaged for the discovery of new and more efficient methods for synthesizing various dithiocarbonates[20-28]by the use of easily available and cost-effective reagents like carbon dioxide and carbon disulfide.

In this communication to the journal, we are reporting an effective and novel synthetic method for symmetric trithiocarbonates out of the various alkyl/aryl-alkyl halides by using the least possible amount of $Cs_2CO_3$ and $CS_2$.

## EXPERIMENTAL

### Chemical

All reagent used in the research were procured by Merck. Products formed in the reaction were diagnosed by collating the obtained data with the existing compounds.


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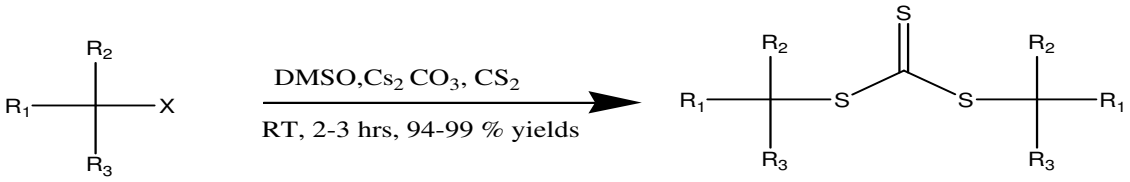
**Instruments**

Infra-Red spectra range (4000-200cm$^{-1}$) was registered by MB-FTIR spectrophotometer and$^{1}$HNMR data of the compounds was registered on Bruker Advance DPX spectrometer at a frequency of(400 MHz) with $CDCl_3$ as solvent & Tetra methyl Silane as standard. Analysis of the various elements in the compounds was registered on Carlo-Erba EA 1110 C,H,N,O,S analyzer and agrees approximately with the calculated values. The products were characterized by collating the data obtained along with that in the literature.

**Reaction**




X=Cl, Br

**Scheme 1**

**General Process**

The dialkyl-,diaryl-alkyl- trithiocarbonates (**1-6**) were prepared at room temperature under ordinary airy conditions. 2 mmols of Carbon disulphide and Caesium Carbonate respectively were added in 6.0 ml of DMSO followed by stirring continuously for 20 minutes. After 20 minutes trithiocarbonate anion formed indicated by the red color solution. To this reaction mixture was then added 2 mmols of allyl bromide and then the reaction mixture was stirred for 2-3 hrs at room temperature and pressure. The color of the reaction mixture turned yellow, thereby indicating the occurrence of the reaction. The process was supervised continuously and simultaneously the product formation was ascertained with the help of TLC. After the completion of the reaction process, the reaction mixture was poured into distilled water and extracted thrice by using ethyl ethanoate. Various trithiocarbonates were obtained taking different alkyl and aryl-alkyl halides respectively. The trithiocarbonate derivatives formed in high yield are given in Table-1.

Table-1: Synthesis of Various Trithiocarbonate Derivatives (1-6)

| Compound | $R_1$ | $R_2$ | $R_3$ | Time (in hrs) | Yield % |
|---|---|---|---|---|---|
| 1 | Vinyl | H | H | 2.5 | 96 |
| 2 | Phenyl | H | H | 3.0 | 99 |
| 3 | Methyl | H | H | 2.5 | 98 |
| 4 | Propyl | H | H | 2.0 | 99 |
| 5 | Ethyl | H | H | 2.5 | 94 |
| 6 | Phenyl | Me | H | 3.0 | 96 |

## RESULTS AND DISCUSSION

Symmetrical trithiocarbonates**1-6** (Table-1) were prepared from corresponding alkyl/aryl-alkyl halide using the minimum amount of $CsCO_3/CS_2$.Carbon disulphide ($CS_2$) and Caesium Carbonate ($Cs_2CO_3$) were added in DMSO in equimolar ratio resulting in the production of negatively charged trithiocarbonate anion on continuous stirring[1]. After this several alkyl/aryl-alkyl halides were added and various trithiocarbonate derivatives were prepared profitable (Scheme-1). The mechanism of this reaction is proposed in (Scheme-2).

**Data Analysis of Trithiocarbonates Derivatives (1-6)**

**Bisdiallyltrithiocarboante (1) Husk Color Oil**

NMR $^{1}$H; (400 MHz, $CDCl_3$, ppm) δ = 4.15(doublet 4H), 5.20(doublet 2H), 5.31 (2H doublet), 5.78-5.86 (2H multiplet), IR (KBr pallet, cm$^{-1}$) 1065 (C=S), $^{13}$C NMR ($CDCl_3$,100 MHz, ppm) δ =39.48, 119.83,

131.11, 22.48; Elemental analysis for $C_7H_{10}S_3$: element, found (calculated) %; C, 43.12 (44.21); H, 4.90 (5.26), S, 51.02 (50.52). Molecular mass of $C_7H_{10}S_3$= 190.35

**Bisdibenzyltrithiocarboanate(2)**
Pale yellowish oil;$^1$H NMR (400 MHz, $CDCl_3$, ppm) δ=4.68(4H singlet),7.30-7.40 (10H multiplet), IR (KBr pallet, $cm^{-1}$)1065 (C=S), $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ =41.62, 128.34, 128.58, 128.80, 134.99, 222.26; Elemental analysis for $C_{17}H_{18}S_3$ element, found(calculated); C, 62.34 (62.06); H, 4.75 (4.82); S= 32.45 (33.10). Molecular mass of $C_{17}H_{18}S_3$ = 318.52

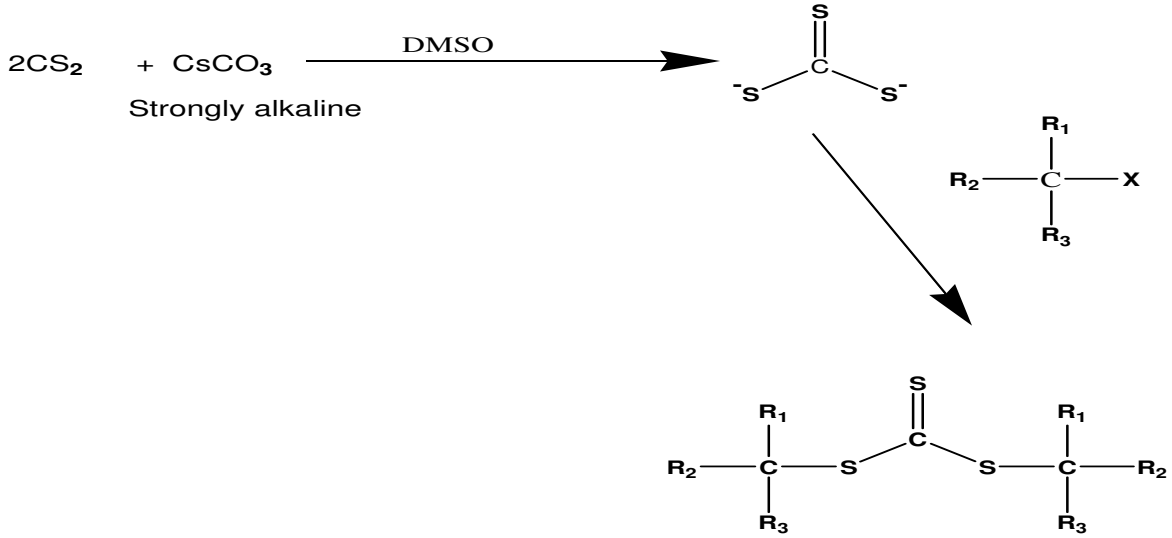
**Bis diethyl trithiocarbonate (3)**
Light yellowish oil; $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ =1.48 (6H t), δ =3.48 (4H, q), IR (KBr pallet, $cm^{-1}$)1068 (C=S), $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ =12.94, 30.98, 223.04; Elemental analysis for $C_5H_{10}S_3$: element, found (calculated)%; C, 33.03 (33.14); H, 5.88(6.02); S 58.83 (57.83). Molecular mass of $C_5H_{10}S_3$ = 166.33

**Bisdibutyltrithiocarbonate (4)**
Yellowish oil; $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ =0.97(6H triplet), 1.48-1.62(4H multiplet), 3.41(4H triplet); IR (KBr pallet, $cm^{-1}$)1052 (C=S); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ =13.60, 21.97, 30.05, 36.55, 224.63; Elemental analysis for $C_9H_{18}S_3$:element, found(calculated)%; C, 46.64 (48.64); H,8.98 (8.10); S, 45.26 (43.24). Molecular mass of $C_9H_{18}S_3$ = 222.43

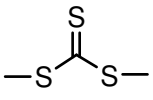
**Bisdipropyltrithiocarbonate (5)**
Yellowish oil;$^1$H NMR (400 MHz, $CDCl_3$, ppm) δ =1.48 (6H t), δ =3.48(4H quintet), IR (KBr pallet, $cm^{-1}$)1065 $cm^{-1}$ (C=S), ), $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ =12.94, 30.98, 223.04; Elemental analysis for $C_7H_{14}S_3$: element, found (calculated)%; C, 42.94 (43.29); H, 8.72 (7.2); S,47.08 (49.48). Molecular mass of $C_7H_{14}S_3$ = 194.38

**Bis(1-phenyl ethyl) Trithiocarbonate (6)**
Pale yellowish oil;$^1$H NMR (400 MHz, $CDCl_3$, ppm) δ =1.82 (6H doublet), 5.39(2H quintet), 7.20-7.45 (10H multiplet);IR (KBr pallet, $cm^{-1}$)1070, 1449, 1493, 1596 $cm^{-1}$ (C=S), $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ =21.41, 50.10, 127.25, 127.68, 143.22, 220.19; Elemental analysis for $C_{17}H_{18}S_3$:element, found (calculated)%; C 63.21 (64.15); H, 4.96 (5.66); S, 31.18 (30.18). Molecular mass of $C_{17}H_{18}S_3$ = 318.52

**Reaction Mechanism**




[$R_1$= Methyl, Ethyl, Propyl, Vinyl, Phenyl; $R_2$= H, Me; $R_3$= H]
Scheme-2

The structures of the compounds**1-6** were derived from their elemental analysis, IR and $^{1}$HNMR analysis. IR peak ranging from1065-1070cm$^{-1}$ informed about C=S stretching which confirmed the presence of C=S in the products formed in the reaction.$^{13}$C NMR showed resonances around δ =220 ppm gives insight that there is the presence of  moiety in the product formed. $^{1}$H NMR of various compounds gave an insight of various bonds in the compound which was in good correlation with the existing compounds.

## CONCLUSION

To conclude, an effective, cheaper, greener and better method for synthesizing Dialkyl/Diaryl-alkyl trithiocarbonates derivatives using $CS_2$, $Cs_2CO_3$ in DMSO at room temperature and pressure has been suggested. The special advantage of this method includes normal reaction conditions, room temperature, easy separation, less time and excellent yield.

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