A Convenient Synthesis of Thiol, Trithiocarbonate and Disulfide

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Abstract

Synthesis of unsymmetrical trithiocarbonate sulfonate salt, along with disulfide, thiol and symmetrical trithiocarbonate from 3-mercapto-1-propane-sulfonicacid, sodium salt with, without of phase transfer catalyst and under various reaction conditions are described. The obtained compounds having divergent usefulness in RAFT polymerization, sulfonyl preparation and having capable of binding in a multidentate fashion to soft transition metal ions.

Keywords

Symmetrical and unsymmetrical trithiocarbonate, disulfide, thiol, sulfonate salts.

INTRODUCTION

The industrial demand for novel synthetic materials with specific properties is constantly growing. From an academic point of view, this has resulted in tremendous effort being put into the research and development of new methods of polymerization that yield polymers with tailored structures and the desired properties. Preparation of polymers with controlled architectures can be achieved by making use of controlled polymerization techniques such as ionic polymerization, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and lately, (RAFT) reversible addition fragmentation chain transfer polymerization. Of all these methods, RAFT polymerization is often reported as being the most
versatile, as it is fairly tolerant to impurities and can be used with a wide range of monomers. The control in RAFT-mediated polymerization is achieved by using trithiocarbonate compounds.\textsuperscript{4-6} Usually, thiol in presence of CS\textsubscript{2} and halides are used for synthesis of trithiocarbonate.\textsuperscript{2,7-9}

**Present Work:**

This present article deals with the preparation of trithiocarbonate salt (1) from commercially available, water soluble, sodium salt of 3-mercapto-1-propane-sulfonic acid in presence of carbon disulfide and NaOH, which is stable intermediate and stored in solution. The salt 1 reacts with bromo compounds 2 gives unsymmetrical 3 (organic salt). The stability of 3 depends on bromo substrate and reaction conditions. In presence of phase transfer catalyst 3 gives thiol (4), without PTC at room gives symmetrical trithiocarbonate (5), and water-soluble sulfonate polymer (6) and without PTC under heating conditions disulfide (7). (Scheme-1).

![Scheme-1](Image)
When intermediate, trithiocarbonate sodium salt (1) reacts with primary bromide (2a-2d), secondary bromide (2e-2f) and tertiary bromide (2g) in presence of catalytic amount of phase transfer catalyst, gives unsymmetrical salt (3), which subsequently cleaved to give thiol (4a-4g). When bromo compounds not having beta phenyl group (2h-2j) gives unsymmetrical trithiocarbonate salt (3h-3j). Under this condition, it is observed that nitrile (4d) was hydrolyzed to amide and the methyl ester (4f) was saponified to corresponding acid. (Table-1).

### Table-1, with PTC

| entry | Substrate | R₁      | R₂ | R₃      | unsym-TTC (3) | yield | Thiol (4) | yield |
|-------|-----------|---------|----|---------|---------------|-------|-----------|-------|
| 1     | 2a        | MeOC₂H₄OCH₂ | H  | H       | 4a            | 65    |           |       |
| 2     | 2b        | CH₂COOH  | H  | H       | 4b            | 78    |           |       |
| 3     | 2c        | COOH     | H  | H       | 4c            | 72    |           |       |
| 4     | 2d        | CN       | H  | H       | 4d            | 72    |           |       |
| 5     | 2e        | COOH     | H  | CH₃     | 4e            | 73    |           |       |
| 6     | 2f        | COOCH₃   | H  | CH₃     | 4f            | 84    |           |       |
| 7     | 2g        | COOH     | CH₃| CH₃     | 4g            | 63    |           |       |
| 8     | 2h        | Ph       | H  | CH₃     | 3g            | 95    | 4h        | 0     |
| 9     | 2i        | 4-Br-Ph  | H  | H       | 3h            | 98    | 4i        | 0     |
| 10    | 2j        | 4-OMe-Ph | H  | H       | 3j            | 95    | 4j        | 0     |

When intermediate trithiocarbonate sodium salt (1) reacts with substrate (2e,2g-2k) gives respective symmetrical trithiocarbonate (5e, 5g-5k) along with polymer sodium sulfonate salt (6). The compound 6 is freely soluble in water, and its structure is confirmed by single crystal data. (Table-2).
When intermediate, trithiocarbonate sodium salt (1) reacts with primary bromide (2a), secondary bromide (2h-2k) under heating condition gives corresponding disulfide (7a, 7h-7k) at pH 14 by extracting with organic solvents, upon acidification (pH4) of aqueous layer, respective thiols (4a, 4h-4k) were isolated (table-3). This method is superior for synthesis of disulfide in odor free environment, over its preparation from sulfide,10-11 halides,12-13 and metal sulfur.14 The PTC method as well as heating (80°C) method are superior for thiol synthesis over reported methods from halide15-16 and in particular from thiourea17 under basic condition, and by reacting alcohol with Lawesson’s reagent18-19.

Table-2, without PTC at room temperature

| entry | Substrate | R_1 | R_2 | R_3 | sym-TTC (5) | yield | Disulfide (7) | yield |
|-------|-----------|-----|-----|-----|-------------|-------|--------------|-------|
| 1     | 2e        | COOH| H   | CH₃ | 5e          | 91    |              |       |
| 2     | 2g        | COOH| CH₃ | CH₃ | 5g          | 62    |              |       |
| 3     | 2h        | Ph  | H   | CH₃ | 5h          | 80    |              |       |
| 4     | 2i        | 4-Br-Ph | H       | H   | 5i          | 70    |              |       |
| 5     | 2j        | 4-OMe-Ph | H       | H   | 5j          | 78    |              |       |
| 6     | 2k        | 4-Cl-Ph | H       | H   | 5k          | 80    |              |       |

Table-3, without PTC at heating

| entry | Substrate | R_1   | R_2 | R_3 | Thiol (4) | yield | Disulfide (7) | yield |
|-------|-----------|-------|-----|-----|-----------|-------|--------------|-------|
| 1     | 2a        | MeOC₂H₄OCH₂ | H   | H   | 4a        | 44    | 7a           | 42    |
| 2     | 2h        | Ph    | H   | CH₃ | 4h        | 36    | 7h           | 40    |
| 3     | 2i        | 4-Br-Ph | H   | H   | 4i        | 40    | 7i           | 38    |
| 4     | 2j        | 4-OMe-Ph | H   | H   | 5j        | 38    | 7j           | 36    |
| 5     | 2k        | 4-Cl-Ph | H   | H   | 4k        | 42    | 7k           | 40    |
MECHANISM:

PART-1: The unsymmetrical trithiocarbonate (3) in equilibrium as cyclic sulfone (C7) and thiolate ion (Ta). In presence of PTC catalyst, the equilibrium shift forwards, as primary bromide substrate (2a-2c), secondary bromide substrate (2d-2f) tertiary bromide substrate (2g) gives thiols, where sodium thiolate ion (Ta) gives thiols (4a-4e and 4g) on acidification. In case of substrate with beta phenyl groups (2h-2j), the equilibrium is backward in undissociated stage (3h-3j) and not given any thiols. It is observed that PTC preventing the self-coupling of thiolate ion (Ta) to form disulfide (7) and preventing chain propagation reaction i.e., attaching on another molecule of 3 in the formation of 6. (scheme-2)

PART-2: without PTC catalyst, the sodium thiolate ion (Ta) (initiation) attacks another molecule of 3 to give the symmetrical trithiocarbonate (TTC) 5 and 3-mercapto-1-propane-sulfonicacid thiolate ion (Tb), as soon it forms, it will attack another molecule 3 to give the stable undissociated di sodium salt (6) by liberating sodium thiolate ion (Tc), so that propagation of reaction goes on until consumption of 3. The aliquot workup shows symmetrical trithiocarbonate (3h and 3i), which disappears after 12 h at room temperature. It is also confirmed that disulfide (DS) is not forming from trithiocarbonate (TTC) by doing independent reaction. (scheme-2).

PART-3: without PTC and under heating condition (80°C), thiol (4) formation takes place along with self-coupling of sodium thiolate ion (Ta) to gives the disulfide (7) in all cases. On prolonging the reaction time, exclusively disulfide product (7k) were isolated. Symmetrical trithiocarbonate (5) trace and disodium salt formation (6) is not detected under heating condition (scheme-2).
To understand the formation of sulfonate salt polymer 6 and its affecting the overall stability of unsymmetrical trithiocarbonate 3, and symmetrical trithiocarbonate 5, we carried out reaction by using one carbonless, ethane mercaptan sulfonate sodium salt as starting material and repeated the same sequence of reactions. After obtaining the stable intermediate 8, we treated with...
substrate 2b, 2e and 2h in presence of PTC and obtained expected thiol 4b, 4e and 9h in good to excellent yields. However, in absence of PTC, the substrates 2b and 2e (having acid group) gives stable unsymmetrical trithiocarbonate 9b and 9e in excellent yield. The phenyl substrate 2h gives 5h in 60% yield along with 11% undissociated 9h. (Table-4)

Table-4, with PTC /without PTC at room temperature by using C2 Sulfonate salt.

| entry | Substrate | R1          | R2  | R3  | Condition | unsym-TTC (9), % | Thiol (4), % | sym-TTC (5), % |
|-------|-----------|-------------|-----|-----|-----------|-----------------|---------------|----------------|
| 1     | 2b        | CH₂COOH     | H   | H   | PTC       | 0               | 4b            | 0              |
| 2     | 2e        | COOH        | H   | CH₃ | PTC       | 0               | 4e            | 0              |
| 3     | 2h        | Ph          | H   | CH₃ | PTC       | 9h, 98%         | 0             | 0              |
| 4     | 2b        | CH₂COOH     | H   | H   | PTC       | 9b, 90%         | 0             | 0              |
| 5     | 2e        | COOH        | H   | CH₃ |           | 9e, 98%         | 0             | 0              |
| 6     | 2h        | Ph          | H   | CH₃ |           | 9h, 11%         | 0             | 5h, 60%        |

The more stability of 9 can be explained due to its intermediate C6 having multiple heteroatoms is less stable due to six membered cyclic system than stable than C7 having seven membered rings. It is noteworthy to mention insoluble at pH14, sulfonate salt polymer (10) (corresponding to 6) is not formed during the reactions. This Carbons-2 sulfonic acid method is useful for the synthesis of thiocarbonate (9), with acid groups. (Scheme-3)
All new compounds were isolated as air and moisture-stable solids. All compounds were fully characterized using $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy and elemental analysis. Organic salts are
freely soluble in polar organic solvents DMSO and DMF and moderately soluble in methanol and ethanol, and insoluble in most organic solvents. The compound 6 is freely soluble in sat. NaHCO$_3$, pH = 9, 10% HCl, water and dmso. Sodium salt of Trithiocarbonate (3) can be useful for transfer surfactants in emulsion polymerizations and symmetrical trithiocarbonate (5) for sulfonyl chloride synthesis$^{21}$. These compounds (5 and 7) possess multiple sulfur atoms and are thus capable of binding in a multidentate fashion to soft transition metal ions.$^{22-24}$ A reaction of these ligands with late transition metal ions is a current focus in our laboratory.

**Conclusions**

We have prepared a series of new unsymmetrical and symmetrical trithiocarbonate, thiol and disulfide compounds containing different other functional groups by using of commercially available, water soluble, mercaptan salt. The synthetic procedure is straightforward, and the products are obtained in good to excellent yields without any chromatographic purification. Excellent solubility properties and the presence of electron donor groups on arms of trithiocarbonate described herein may be advantageous in applications RAFT polymerization and ligand preparation using transition metals.

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**Declaration of Competing Interest** The authors declare that they have no known competing financial interests.

**Data and materials availability:** Requests for materials should be addressed to Sudershan Gondi (gondisr@gmail.com)
EXPERIMENTAL SECTION:

3-mercapto-1-propane-sulfonicacid, sodium salt and carbon disulfide were obtained from Acros and Aldrich respectively. All other materials were reagent grade unless otherwise specified. All reactions were carried out in a dry nitrogen atmosphere. 1H and 13C NMR spectra were obtained on a 400-MHz Bruker Avance NMR spectrometer. Infrared spectra were obtained on a Nicolet Magna-IR 560 spectrometer E.S.P. Elemental analyses were obtained with a CE Elantech Thermo-Finnigan Flash 1112 CHN elemental analyzer. Melting points were collected on a TA Instruments DSC 2010 Differential Scanning Calorimeter using a heating rate of 108°C/min and nitrogen as a purge gas.

3-Dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt (1): To a solution of 3-mercapto-1-propane-sulfonicacid, sodium salt, (10.0 g, 56.0 mmol) in 80 mL of water, add freshly prepared (20 mL) of (6.73 g, 168 mmol) NaOH solution. After stirring at room temperature for 30 minutes, add carbon disulfide (3.36 mL, 5.6 mmol) drop wise over a period of 5 minutes. Stir the reaction mixture for overnight (18 h). This is stock solution, which is stable for over months, 15.5 g (56 mmol) in 100 mL. 1.56 g (5.6 mmol) of in situ salt in 10 mL or 1.0 g (3.6 mmol) of in situ salt in 6.45 mL. 1H-NMR (400 MHz, d2o):  δ 3.30-3.26 (t, 2H, J = 7.0 Hz, -CH2SO3), 3.01-2.97 (t, 2H, -CH2S), 2.10-2.07 (m, 2H, -CH2CH2S). 13C-NMR (100.6 MHz, d2o):  δ 50.4 (-CH2SO3), 40.0 (-CH2S), 23.9 (-CH2CH2S). IR (KBr) (wavenumber, cm⁻¹): 3442, 2985 (C-Cs), 1638, 1443, 1408, 1194, 1048 (C=S), 870 (C-Cb). Elemental Analysis, Calcd for C4H8Na2O3S4: C) 17.39%, H) 2.19%. Found: C) 17.39%, H) 2.19%.
3-(1-Phenyl-ethylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt\textsuperscript{25} (3h):

To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was added 1-bromoethyl benzene (667 mg, 5.6 mmol), in presence of catalytic amount of tetrabutylammonium bromide (20 mg). Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Dilute the reaction mass with water (50 mL), filter, washed with water (50 mL), ether (50 mL) and dry in vacuum to compound 4g as yellow solid (1.25 g, 98%). Mp 282.6°C. \textsuperscript{1}H-NMR (400 MHz, dmso-d6): $\delta$ 7.44-7.42 (d, 2H, $J = 7.2$ Hz, 2,6 Ar-$H$), 7.37-7.33 (t, 2H, $J = 7.0$ Hz, 3,5 Ar-$H$), 7.30-7.27 (t, 1H, $J = 7.0$ Hz, 4-Ar$H$), 5.30-5.24 (q, 1H, $J = 6.8$ Hz, Ar$CHCH_3$), 3.48-3.44 (t, 2H, $J = 7.1$ Hz, -$CH_2SO_3$), 2.50-2.47 (t, 2H, $J = 7.0$ Hz, -$CH_2S$), 1.96-1.88 (m, 2H, -$CH_2CH_2S$) 1.71-1.70 (d, 3H, $J = 7.0$ Hz, Ar$CHCH_3$). \textsuperscript{13}C-NMR (100.6 MHz, dmso-d6): $\delta$ 141.6 (C1-Ar), 129.5 (C2 & C6-Ar), 128.6 (C3 & C5-Ar), 128.4 (C4-Ar), 50.6 (-$CH_2SO_3$), 50.6 (Ar-$CH-CH_3$), 36.2 (-$CH_2S$), 24.9 (-$CH_2CH_2S$), 22.0 (Ar-$CH-CH_3$). IR (KBr) (wavenumber, cm$^{-1}$): 3509, 2929 (C-C$\equiv$S), 1627, 1439, 1173, 1057 (C=S), 820 (C-Cb). Elemental Analysis, Calcd for C$_{12}$H$_{15}$NaO$_3$S$_4$: C) 40.97%, H) 4.38%. Found: C) 40.27%, H) 4.68%.

3-(4-Bromo-benzylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt\textsuperscript{26} (3i):

In the manner described above, 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1 sulfonic acid disodium salt was treated with 4-bromo benzyl bromide (0.905 mg, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain compound 3h (1.45 g, 95%). MP 236.6°C, \textsuperscript{1}H-
NMR (400 MHz, dmso-d₆): δ 7.51 (s, 2H), 7.35 (2H), 4.64 (s, 2H), 3.49 (s, 2H), 2.51 (s, 2H), 1.98 (s, 2H). ¹³C-NMR (400 MHz, dmso-d₆): δ 135.8, 132.3, 132.2, 121.8, 50.6, 40.2, 36.5, 24.9
IR (KBr): 3508, 2930, 1630, 736 (medium), 1485, 1217, 1176, 1058, 820 cm⁻¹ (strong).
Elemental Analysis: Calcd: C, 31.21, H, 2.86. Found: C, 30.58, H, 3.26.

After acidification, Sulfonic acid shows Mp 240.82°C. ¹H-NMR (400 MHz, dmso-d₆): δ 7.53-7.51 (d, 2H, J = 7.54 Hz, 3,5 Ar-H), 7.36-7.31 (d, 2H, J = 7.51 Hz, 2,6 Ar-H), 4.65 (s, 2H, ArCH₂S), 3.49-3.47 (d, 2H, J = 6.67 Hz, -CH₂SO₃), 2.50 (s, 2H, -CH₂S), 1.96-1.94 (d, 2H, J = 6.65 Hz, -CH₂CH₂S).
¹³C-NMR (100.6 MHz, dmso-d₆): δ 135.8 (C1-Ar), 132.3 (C2 & C6-Ar), 132.2 (C3 & C5-Ar), 121.6 (C4-Ar), 50.7 (-CH₂SO₃), 40.2 (Ar-CH₂S), 36.6 (-CH₂S), 24.9 (-CH₂CH₂S). IR (KBr) (wavenumber, cm⁻¹): 3513, 2931 (C-Cs), 1627, 1486, 1287, 1173, 1064 (C=S), 817 (C-Cb). Elemental Analysis, Calcd for C₁₁H₁₃BrO₃S₄: C) 31.21%, H) 2.86%. Found: C) 31.28%, H) 3.17%.

3-(4-methoxy-benzylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt²⁶

(3j): In the manner described above, 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1 -sulfonic acid disodium salt was treated with 4-methoxy benzyl chloride (0.562 mg, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain compound 3j (1.3 g, 95%), ¹H-NMR (400 MHz, dmso-d₆): δ 7.30 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 4.59 (s, 2H), 3.71 (s, 3H), 3.47 (t, J = 7.3 Hz, 2H), 2.58-243 (m, 2H), 1.93 (t, J = 7.3 Hz, 2H), ¹³C-NMR (400 MHz, dmso-d₆): δ 224.2, 159.2, 130,9, 127.0, 114.4, 55.5, 50.3, 40.5, 35.9, 24.6.
bis[2-(2-methoxyethoxy)-ethanethiol]27 (4a): To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was added 1-bromo-2-(2-methoxyethoxy)-ethane, (0.66 g, 3.6 mmol) in presence of catalytic amount of tetrabutyl ammonium bromide (20 mg). Stir the reaction mixture for overnight (12 h). Dilute the reaction mixture with water (50 mL) and extract with ether (50 mL). to remove the impurities. The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (50 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over MgSO₄ and filter. The filtrate was concentrated to give thiol as residual oil. (640 mg, 65%). ¹H-NMR (400 MHz, CDCl₃): δ 3.63–3.60 (t, 4H, J = 6.1 Hz, CH₃O-CH₂-CH₂O-), 3.56–3.54 (t, 2H, J = 4.5 Hz, -OC₃H₂CH₂S), 3.38 (s, 3H, -OC₃H₃), 2.73–2.68 (m, 2H, -CH₂S), 1.61–1.57 (t, 1H, SH, J = 8.2 Hz, -CH₂S). ¹³C-NMR (100.6 MHz, CDCl₃): δ 71.3 (CH₃O-CH₂-CH₂O-), 70.6 (CH₃O-CH₂-CH₂O-), 69.8 (-OCH₂CH₂S), 58.4 (-OCH₃), 29.7 (-CH₂S). IR (KBr) (wavenumber, cm⁻¹): 2877 (C-C), 1454, 1355, 1293, 1198, 1140 (C=S), 735 (C-Cb). Elemental Analysis, Calcd for C₅H₁₂O₂S: C) 44.09%, H) 8.88%. Found: C) 44.01%, H) 9.19%.

3-Mercaptopropanoic acid28 (4b): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was treated 3-bromopropanoic acid, (0.55 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain product as residual oil (296 mg, 77.8%). ¹H- NMR (400 MHz, CDCl₃): δ 11.67 (br-s, 1H, COOH), 2.77-267 (m, 4H, HSC₃H₂CH₂), 1.69-1.67 (t, J = 7.8 Hz, SH). NMR (400 MHz, d₂O): δ 2.657-261 (m, 4H, HSC₃H₂CH₂), ¹³C-NMR (100.6 MHz, CDCl₃): δ 178.0 (COOH), 38.1
(HSCH₂CH₂), 19.1 (HOOCCH₂CH₂). ¹³C-NMR (100.6 MHz, d₂O): ¹ δ 178.6 (COOH), 38.2 (HSCH₂CH₂), 19.3 HOOCCH₂CH₂).

2-Mercaptoacetic acid²⁹ (4c): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 2-bromo acetic acid, (0.5 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtained product as residual oil (235 mg, 71.6%). ¹H-NMR (400 MHz, CDCl₃): δ 3.06 (s, 2H, HSC₃H₂COOH), ¹³C-NMR (100.6 MHz, d₂O): δ 178.6 (COOH), 29.0 (HSCH₂COOH),

2-Mercapto-2-methyl-propanamide³⁰ (4d): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 2-bromo propionitrile, (0.48 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain product as residual oil (270 mg, 72.5%). ¹H-NMR (400 MHz, d₂O): δ 3.76-3.71 (m, 1H, -C₃H₇), 1.46-1.51 (m, 3H, -CH₃H₃). ¹³C-NMR (100.6 MHz, d₂O): δ 178.2 (CONH₂), 42.9 (-CH₃H), 17.6 (-CH₃H₃).

2-Mercapto-propanoic acid³¹ (4e): To a 6.45 mL (1.0 g, 3.6 mmol) situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was added 2-bromopropanoicacid, (560 mg, 3.6 mmol) in presence of catalytic amount of tetra butyl ammonium bromide (20 mg). Stir the reaction mixture for overnight (12 h). Dilute the reaction mixture with water (50 mL) and extract with ether (50 mL) to discard the impurities. The aqueous layer on acidified with concentrated HCl to pH = 2, then extract with ether (50 mL X 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was
concentrated to give product as residual oil (280 mg, 73%). $^1$H-NMR (400 MHz, CDCl$_3$): $^\delta$ 11.14 (br-s, 1H, COOH), 3.58-3.50 (m, 1H, HSC$_2$H$_3$), 2.25-2.23 (s, $J = 7.8$ Hz, 1H, -SH) 1.55-1.53 (d, $J = 7.8$ Hz, HOOCCH$_2$H$_3$). $^{13}$C-NMR (100.6 MHz, d$_2$O): $^\delta$ 180.0 (COOH), 35.5 (HSCH$_2$H$_3$), 20.6 (HOOCCH$_2$H$_3$).

2-Mercapto-propanoic acid$^{31}$(4e): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonic acid di sodium salt was treated methyl, 2-bromopropionoate, (0.55 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain product as residual oil (327 mg, 84%). NMR values are consistent with the reported values.

2-Mercapto-2-methyl-propanoic acid$^{32}$ (4g): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 2-bromo-2-methyl propanoic acid, (0.6 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain product as solid. (270 mg, 63%). Mp 194-196$^\circ$C. $^1$H-NMR (400 MHz, dms-o-d$_6$): $^\delta$ 12.74 (br-s, 1H, COOH), 3.45 (s, 1H, HS), 1.44 (s, 6H, HSC(CH$_3$)$_2$) $^{13}$C-NMR (100.6 MHz, d$_2$O): $^\delta$ 180.0 (COOH), 57.5 (HSCH$_2$H$_3$), 30.7 (HOOCCH$_2$H$_3$)$_2$). IR (KBr) (wavenumber, cm$^{-1}$): 298010, 2654 (C-Cb), 1688, 1464, 1289, 1165, 1113 (C=S), 809 (C-Cb).

3-(3-Sulfo-propylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid, di sodium salt (6):

To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was added 2-bromo propanoic acid,
(430 mg, 3.6 mmol). Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Filter the yellow solid, suspended in acetone, filter and dry in vacuum to give compound 6 (550 mg, 44.1%). Mp >250°C. ¹H-NMR (400 MHz, dms-o-d₆): δ 3.50-3.47 (t, 4H, J = 6.8 Hz, -CH₂SO₃), 2.55-2.51 (t, 4H, J = 7.2 Hz, -CH₂S), 1.96-1.93 (t, 4H, J = 7.0 Hz, -CH₂CH₂S). ¹³C-NMR (100.6 MHz, dms-o-d₆): δ 50.6 (-CH₂SO₃), 36.2 (-CH₂S), 24.9 (-CH₂CH₂S). ¹H-NMR (400 MHz, d₂o): δ 3.50-3.47 (t, 2H, J = 7.2 Hz, -CH₂SO₃), 2.96-2.92 (t, 2H, J = 7.2 Hz, -CH₂S), 2.13-2.05 (m, 2H, -CH₂CH₂S). ¹³C-NMR (100.6 MHz, d₂o): δ 50.0 (-CH₂SO₃), 35.2 (-CH₂S), 23.6 (-CH₂CH₂S). IR (KBr) (wavenumber, cm⁻¹): 3510, 2931 (C-Cs), 1626, 1418, 1216, 1172, 1049 (C=S), 828 (C-Cb). Elemental Analysis, Calcd for C₇H₁₂BrNa₂O₆S₅: C) 21.10%, H) 3.05%. Found: C) 21.14%, H) 3.70%. Single crystal data confirmed the structure.

2-mercapto propanoic acid trithiocarbonate³³ (5e): The aqueous layer on acidified with concentrated HCl to pH 2, Filter the yellow solid and dry in vacuum to give trithiocarbonate 5e (410 mg, 91%). NMR values are consistent with the reported values.

2,2’-[(Thioxomethylene)disulfanyl]bis(2-methylpropanoic acid)⁷ (5g): In the manner described above, 2.5 g (14 mmol) of 3-mercapto-1-propane-sulfonic acid sodium salt was treated with sodium hydroxide (1.68 g, 42 mmol), carbon disulfide (1.06 g, 0.84 mL, 14 mmol) followed by 2-bromo-2-methyl-propanoic acid (2.34 g, 14 mmol). After the completion of reaction (12h), filtered to remove solid 6 and extracted the aqueous layer on acidified with conc HCl to pH 2, Filter the yellow solid, suspended in hexane, filter and dry in
vacuum to give trithiocarbonate 5g (1.22 g, 62%). Mp = 186.59°C. $^1$H-NMR (400 MHz, dmsodo): $\delta$ 1.58 (s, 12H, S-C(CH$_3$)$_2$-COOH). $^{13}$C-NMR (100.6 MHz, dmso-d$_6$): $\delta$ 173.9 (C=O), 57.0 (S-C(CH$_3$)$_2$-COOH), 25.7 (S-C(CH$_3$)$_2$-COOH). IR (KBr) (wavenumber, cm$^{-1}$): 2985 (C-Cs), 1593, 1700 (C=O), 1285, 1063 (C=S), 805 and 761 (C-Cb). Elemental Analysis, Calcd for C$_9$H$_{14}$O$_4$S$_3$: C) 38.28%, H) 5.00%. Found: C) 38.71%, H) 5.04%.

**Carbonotrithioic acid, bis(1-phenylethyl) ester**$^{34}$ (5h): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 1-bromo ethyl benzene (0.67 g, 3.6 mmol). After completion of reaction (12 h), filtered to remove solid 6 and extracted with ether 50 mL x 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give trithiocarbonate 5h (460 mg, 80%). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (m, 5H, Ph), 5.32 (q, 1H, $J$ = 7.8 -SCH(CH$_3$), 1.73-1.54 (m, 3H, (S-C(CH$_3$)$_2$) $^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ 140.9, 128.5, 127.6, 127.6, 49.9 (S-C(H(CH$_3$)$_3$), 21.5 (S-C(CH$_3$)$_3$).

**Carbonotrithioic acid, bis[(4-bromophenyl) methyl] ester**$^{35}$ (5i): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 4-bromobenzylbromide (0.67 g, 3.6 mmol). After the completion of reaction (12h), filtered to remove solid 6 and extracted the aqueous layer with ether (50 mL x 2), and the organic layer was
washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated gives trithiocarbonate 5i (560 mg, 70%). Mp = 93.27°C. The compounds 5i is confirmed by single crystals data. ¹H-NMR (400 MHz, CDCl₃): δ 7.44 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.54 (s, 2H, -SC₆H₄Ph). ¹³C-NMR (100.6 MHz, CDCl₃): δ 134.0, 131.7, 130.6, 121.7, 40.6 (S-CH₃Ph). IR (KBr): 2920, 1895, 1402, 720 (medium), 1483, 1058, 1009, 795 cm⁻¹ (strong). The impurity cyclic bromine is also confirmed by single crystals data.

**Carbonotrithioic acid, bis[(4-methoxyphenyl) methyl] ester** (5j): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was treated 4-methoxybenzylchloride (563 g, 3.6 mmol). After the completion of reaction (12h), filtered to remove solid 6 and extracted the aqueous layer with ether (50 mL x 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated gives trithiocarbonate 5j (490 mg, 78%). ¹H-NMR (400 MHz, CDCl₃): δ 7.26 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.57 (s, 2H, -SC₆H₄Ph), 3.80 (s, 3H, (PhOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 223.1 (C=S), 159.1, 130.5, 126.6, 114.1, 55.2, 41.1.

**Carbonotrithioic acid, bis[(4-chlorophenyl) methyl] ester** (5k): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was treated 4-chlorobenzylchloride
(577 mg, 3.6 mmol). After the completion of reaction (12 h), filtered to remove solid 6 and extracted the aqueous layer with ether (50 mL x 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated gives trithiocarbonate 5k (515 g, 80%). Melting point is 55-57°C. ¹H-NMR (400 MHz, cdcl₃): δ 7.25 (s, 4H), 4.55 (s, 2H). ¹³C-NMR (400 MHz, cdcl₃): δ 133.6, 133.5, 130.5, 128.8, 40.5. IR (KBr): 2922, 1894, 1404, 722 (medium), 1489, 1091, 1057, 796 cm⁻¹ (strong). The compounds 5k is confirmed by single crystals data.

**bis[2-(2-methoxyethoxy)-ethyl]-disulfide (7a):** To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 6, was added compounds 2a (0.66 g, 3.6 mmol) and heat at 80°C for 2h. After completion of reaction dilute the reaction mixture with water (50 mL) and extract with ether (25 mL x 2). Wash the ether layer with wash (50 mL), brine solution (50 mL), dried over MgSO₄ and filter. The filtrate was concentrated to obtain disulfide 7a as residual oil (202 mg, 42 %). ¹H-NMR (400 MHz, cdcl₃): δ 3.74-3.61 (m, 8H, CH₃O-CH₂-CH₂O-), 3.55-3.53 (dd, 4H, J = 2.5 Hz and 3.8 Hz, -OCH₂CH₂S), 3.38 (s, 6H, -OC₂H₃), 2.78-2.75 (t, 4H, J = 6.9 Hz, -CH₂S). ¹³C-NMR (100.6 MHz, cdcl₃): δ 71.8 (CH₃O-CH₂-CH₂O-), 71.0 (CH₃O-CH₂-CH₂O-), 70.2 (-OCH₂CH₂S), 59.7 (-OCH₃), 31.7 (-CH₂S). IR (KBr) (wavenumber, cm⁻¹): 2876 (C-Cs), 1354, 1275, 1198, 1100 (C=S), 733 (C-Cb). Elemental Analysis, Calcld for C₁₀H₂₂O₄S₂: C) 44.42%, H) 8.20%. Found: C) 44.29%, H) 8.19%.

**bis[2-(2-methoxyethoxy)-ethanethiol27 (4a):** The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine
solution (50 mL), dried over MgSO₄ and filter. The filtrate was concentrated to give thiol 4a as residual oil. (216 mg, 44%).

**bis(1-phenylethyl) disulfide**<sup>38</sup> (7h): To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 6, was added 1-bromo ethyl benzene (0.67 g, 3.6 mmol) and heat at 80°C for 2 h. The reaction mixture was dilute with water and extract with ether (25 mL X 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give disulfide 7i (195 mg, 40%). NMR data is consistent with reported values.

**1-phenylethyl thiol**<sup>39</sup> (4h): The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over MgSO₄ and filter. The filtrate was concentrated to give thiol 4i as residual oil. (170 mg, 36%). NMR data is consistent with reported values.

**Bis(p-bromobenzyl) disulfide**<sup>40</sup> (7i): To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 6, was added 4-bromobenzylbromide (0.9 g, 3.6 mmol) and heat at 80°C for 2 h. The reaction mixture was dilute with water and extract with ether (25 mL X 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give disulfide 7i (138 mg, 38%). NMR data is consistent with reported values.
p-bromobenzyl thiol\textsuperscript{41} (4i): The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over MgSO\textsubscript{4} and filter. The filtrate was concentrated to give thiol 4i as residual oil (290 mg, 40%). NMR data is consistent with reported values.

Bis(p-methoxybenzyl) disulfide\textsuperscript{42} (7j): To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 6, was added 4-methoxybenzylchloride (563 g, 3.6 mmol) and heat at 80\textdegree C for 2 h. The reaction mixture was dilute with water and extract with ether (25 mL X 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give disulfide 7i (200 mg, 36%). NMR data is consistent with reported values.

p-methoxybenzyl thiol\textsuperscript{43} (4j): The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over MgSO\textsubscript{4} and filter. The filtrate was concentrated to give thiol 4i as residual oil. (210 mg, 38%). NMR data is consistent with reported values.

Bis(p-chlorobenzyl) disulfide\textsuperscript{40} (7k): To a 6.45 mL (1.0 g, 3.6 mmol) in situ solution of 6, was added treated with 4-chlorobenzyl chloride (580 mg, 0.0036 mol) and heat at 80\textdegree C for 2 h. The reaction mixture was dilute with water and extract with ether (25 mL X 2), and the organic layer was washed with
water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give 226 mg of disulfide 7k in 40% yield. Melting point is 51-52°C. $^1$H-NMR (400 MHz, cdcl$_3$): δ 7.30-7.28 (d, 2H, J = 8.3 Hz), 7.16-7.14 (d, 2H, J = 8.3 Hz), 3.57 (s, 2H). $^{13}$C-NMR (400 MHz, cdcl$_3$): δ 135.8, 133.3, 130.6, 128.6, 42.4 IR (KBr): 3044, 2907, 1901, 720(medium), 1487, 1092, 1012, 832 cm$^{-1}$ (strong). The compounds 7k is confirmed by single crystals data.

p-chlorobenzyl thiol$^{44}$ (4k): The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over MgSO$_4$ and filter. The filtrate was concentrated to give thiol 4k as residual oil. (238 mg, 42%). $^1$H-NMR (400 MHz, cdcl$_3$): δ 7.25-7.19 (m, 4H) 3.66 (d, 2H, J = 8.3 Hz), 1.75 (s, 1H, J = 8.3 Hz). $^{13}$C-NMR (400 MHz, cdcl$_3$): δ 139.4, 132.6, 129.2, 128.6 28.1. IR (KBr): 3047, 2933, 1997, (medium), 1490, 1264, 1092, 830 cm$^{-1}$ (strong).

3-Dithiocarboxysulfanyl-ethane-1-sulfonic acid disodium salt (8): To a solution of 3-mercapto-1-ethane-sulfonicacid, sodium salt, (2.5 g, 15.2 mmol) in 15 mL of water, add freshly prepared (10 mL) of (1.83 g, 45 mmol) NaOH solution. After stirring at room temperature for 30 minutes, add carbon disulfide (914 uL, 15.2 mmol) drop wise over a period of 5 minutes. Stir the reaction mixture for overnight (18 h). This is stock solution, which is stable for over months, 4.0 g (15.2 mmol) in 25 mL. 400 mg (15.2 mmol) of in situ salt in 2.5mL or 1.0 g (3.8 mmol) of in situ salt in 6.25 mL. IR (KBr) (wavenumber, cm$^{-1}$): 3371, 2985 (C-Cs), 1627, 1443, 1407, 1193, 1048 (C=S), 860 (C-Cb).
Sodium 3-((((2-sulfonatoethyl)thio)carbonothioyl)thio)propanoate (9b): To a 6.25 mL (1.0 g, 3.8 mmol) in situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was added 3-bromo propanoic acid (590 mg, 5.6 mmol), Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Dilute the reaction mass with water (50 mL), filter, washed with water (50 mL), ether (50 mL) and dry in vacuum to compound 9b as yellow solid (1.14 g, 90%). \( ^{1}H\text{-NMR (400 MHz, } d_{2}o): \delta 3.14-3.10 (dd, 2H, J = 5.4 & 3.2 Hz), 2.87-2.83 (dd, 2H, J = 5.0 & 3.2 Hz), 2.76-2.73 (t, 2H, J = 7.2 Hz), 2.45-2.41 (t, 2H, J = 7.1 Hz). \) \( ^{13}C\text{-NMR (400 MHz, } d_{2}o): \) 181.3, 51.4, 37.7, 28.3, 25.9. \( \text{IR (KBr): } 2925, 2105, 1315 (\text{medium}), 3418, 1586, 1562, 1438, 1195, 1058 \text{ cm}^{-1} (\text{strong}). \)

Sodium 2-((((2-sulfonatoethyl)thio)carbonothioyl)thio)propanoate (9e): To a 6.25 mL (1.0 g, 3.8 mmol) in situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was added 2-bromo-propanoic acid (590 mg, 5.6 mmol), Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Dilute the reaction mass with water (50 mL), filter, washed with water (50 mL), ether (50 mL) and dry in vacuum to compound 9e as yellow solid (1.19 g, 98%). \( ^{1}H\text{-NMR (400 MHz, } d_{2}o): \delta 3.41-3.36 (q, 1H, J = 6.7 Hz), 3.12-3.08 (dd, 2H, J= 5.1 & 3.8 Hz), 2.86-2.82 (dd, 2H, J = 6.4 & 2.3 Hz) 1.32-1.30 (d, 3H, J = 7.0 Hz). \) \( ^{13}C\text{-NMR (400 MHz, } d_{2}o): \) 181.5, 51.4, 46.0, 25.7, 18.3. \( \text{IR (KBr): } 1637, 1315, 748 (\text{medium}), 3424, 1585, 1562, 1438, 1195, 1058 \text{ cm}^{-1} (\text{strong}). \)
3-(1-Phenyl-ethylsulfanyltiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt (9h):

To a 6.25 mL (1.0 g, 3.8 mmol) in situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonic acid disodium salt was added 2-bromoethyl benzene (710 mg, 3.8 mmol), Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Dilute the reaction mass with water (50 mL), filter, washed with water (50 mL), ether (50 mL) and dry in vacuum to compound 9h as yellow solid (144 mg, 11%). ¹H-NMR (400 MHz, dmso-d₆): δ 7.31-7.12 (m, 4H), 4.02-4.00 (t, 1H, J = 6.95 Hz), 2.87-250 (m, 4H), 1.46-1.44 (d, 3H, J = 7.0 Hz). ¹³C-NMR (400 MHz, dmso-d₆): δ 144.6, 129.3, 128.0, 127.8, 52.2, 43.6, 27.0, 23.1.

Carbonotrithioic acid, bis(1-phenylethyl) ester³⁴ (5h): The aqueous solution (pH=14) was extracted with Ether, concentrated, dry to obtain the 360 mg in 60% yield.

Repeating same molar reaction in presence of PTC (20 mg) gives 98% yield. (1.28 g) of 9h.

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