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

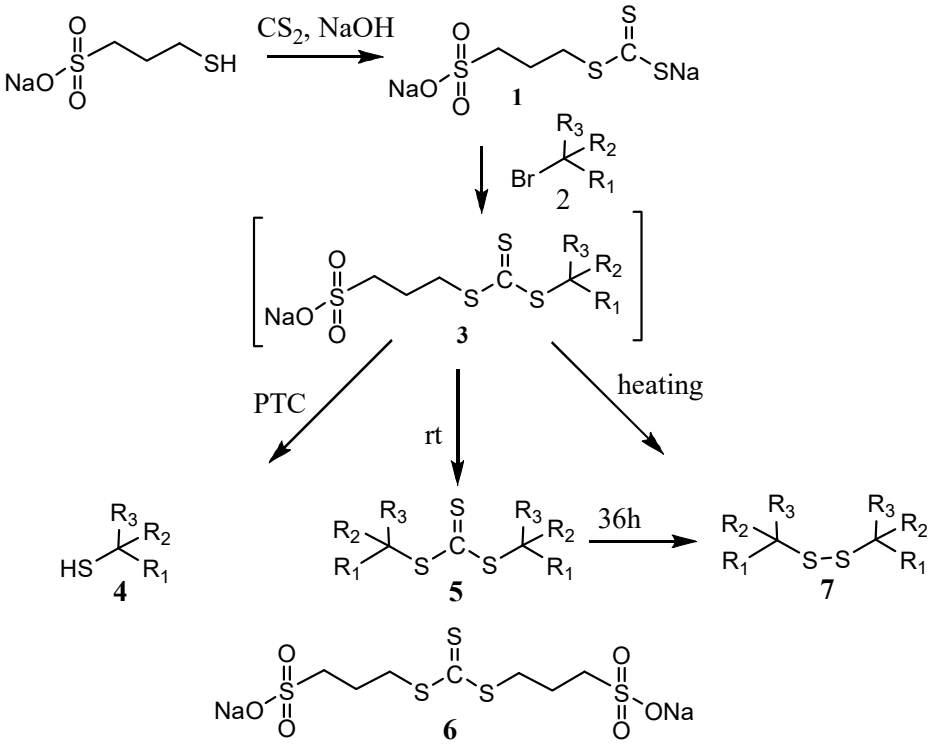
The industrial demand for novel synthetic materials with specific properties is constantly growing. From an academic point of view, this has resulted in tremendous effort being put into the research and development of new methods of polymerization that yield polymers with tailored structures and the desired properties. Preparation of polymers with controlled architectures can be achieved by making use of controlled polymerization[1-2] techniques such as ionic polymerization, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and lately, (RAFT) reversible addition fragmentation chain transfer polymerization.[3] 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.[4-6]. Usually, thiol in presence of CS_2 and halides are used for synthesis of trithiocarbonate.[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



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	R_1	R_2	R_3	unsym-TTC (3)	yield	Thiol (4)	yield
1	2a	$MeOC_2H_4OCH_2$	H	H			4a	65
2	2b	CH_2COOH	H	H			4b	78
3	2c	COOH	H	H			4c	72
4	2d	CN	H	H			4d	72
5	2e	COOH	H	CH_3			4e	73
6	2f	$COOCH_3$	H	CH_3			4f	84
7	2g	COOH	CH_3	CH_3			4g	63
8	2h	Ph	H	CH_3	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 sulfonate salt (**6**). The compound **6** is freely soluble in water, and its structure is confirmed by single crystal data. (table-2).

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	CH_3	5e	91		
2	2g	COOH	CH_3	CH_3	5i	62		
3	2h	Ph	H	CH_3	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		

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 (80ºC) method are superior for thiol synthesis over reported methods from halide[15-16] and in particular from thiourea[17] under basic condition, and by reacting alcohol with Lawesson's reagent[18-19].

Table-3, without PTC at heating

entry	Substrate	R_1	R_2	R_3	Thiol (4)	yield	Disulfide (7)	yield
1	2a	$MeOC_2H_4OCH_2$	H	H	4a	44	7a	42
2	2h	Ph	H	CH_3	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

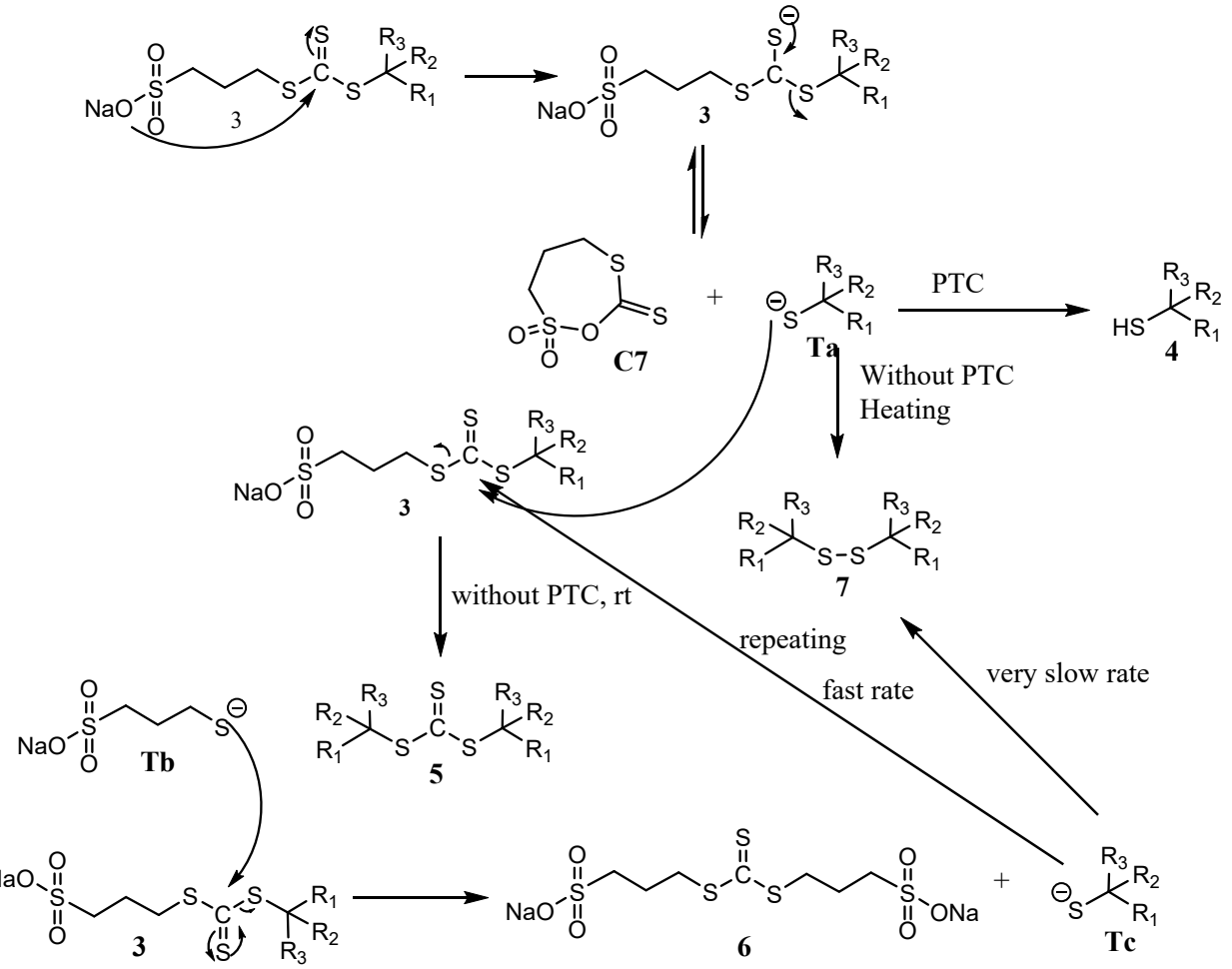
MECHANISM:

PART-1: The unsymmetrical trithiocarbonate (**3**) in equilibrium as cyclic sulfone[20] (**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 ie., 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 after12 h at room temperature. It is also confirmed that disulfide (DS) is not forming from trithiocarbonate (TTC) by doing independent reaction. (scheme-2).

scheme-2



PART-3: without PTC and under heating condition (80ºC), 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).

All new compounds were isolated as air and moisture-stable solids. All compounds were fully characterized using ^{1}H and ^{13}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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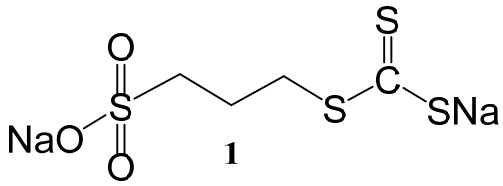
Declaration of Competing Interest The authors declare that they have no known competing financial interests.

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 108ºC/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. ^{1}H-NMR (400 MHz, d_2o): $^{\delta}$ 3.30-3.26 (t, 2H, *J* = 7.0 Hz, -***C*H**$_2$SO$_3$), 3.01-2.97 (t, 2H, *J* = 7.2 Hz, -***C*H**$_2$S), 2.10-2.07 (m, 2H, -C***H*$_2$*C*H$_2$S). ^{13}C-NMR (100.6 MHz, d_2o): $^{\delta}$ 50.4 (-***C***H$_2$SO$_3$), 40.0 (-***C***H$_2$S), 23.9 (-***C***H$_2$*C*H$_2$S)**.** IR (KBr) (wavenumber, cm^{-1}): 3442, 2985 (C-Cs), 1638, 1443, 1408, 1194, 1048 (C=S), 870 (C-Cb). Elemental Analysis, Calcd for $C_4H_6Na_2O_3S_4$: C) 17.39%, H) 2.19%. Found: C) 17.39%, H) 2.19%.



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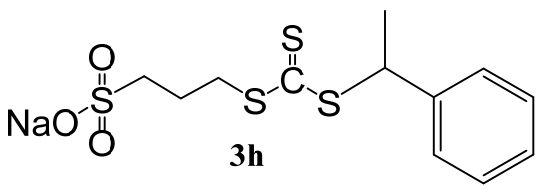
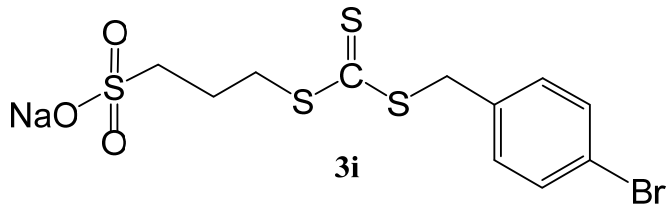
3-(1-Phenyl-ethylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt[25] (3h):



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 282.6ºC. ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 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, ArC***H***CH_3), 3.48-3.44 (t, 2H, *J* = 7.1 Hz, -*C****H***$_2SO_3$), 2.50-2.47 (t, 2H, *J* = 7.0 Hz, -*C****H***$_2$S), 1.96-1.88 (m, 2H, -C***H***$_2$*C*H_2S) 1.71-1.70 (d, 3H, *J* = 7.0 Hz, ArCHC***H***$_3$). ^{13}C-NMR (100.6 MHz, dmso-d_6): $^{\delta}$ 141.6 (***C***1-Ar), 129.5 (***C***2 & ***C***6-Ar), 128.6 (***C***3 & ***C***5-Ar), 128.4 (***C***4-Ar), 50.6 (-***C***H_2SO_3), 50.6 (Ar-***C***H-CH_3), 36.2 (-**C**H_2S), 24.9 (-***C***H_2*C*H_2S), 22.0 (Ar-CH-***C***H_3). IR (KBr) (wavenumber, cm^{-1}): 3509, 2929 (C-Cs), 1627, 1439, 1173, 1057 (C=S), 820 (C-Cb). Elemental Analysis, Calcd for $C_{12}H_{15}NaO_3S_4$: C) 40.97%, H) 4.38%. Found: C) 40.27%, H) 4.68%.

3-(4-Bromo-benzylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt[26] (3i):

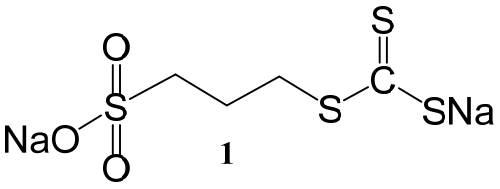


3i

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, ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 7.51 (s, 2H), 7.35 (2H), 4.64 (s, 2H), 3.49 (s, 2H), 2.51 (s, 2H), 1.98 (s, 2H). ^{13}C-NMR (400 MHz, dmso-d_6): $^{\delta}$ 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. ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 7.53-



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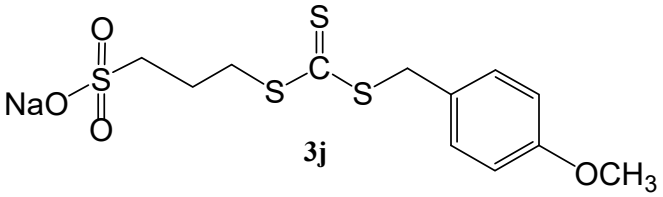
7.51 (d, 2H, *J* = 7.54 Hz, 3,5 Ar-***H***), 7.36-7.31 (d, 2H, *J* = 7.51 Hz, 2,6 Ar-***H***), 4.65 (s, 2H, ArC***H***$_2$S), 3.49-3.47 (d, 2H, *J* = 6.67 Hz, -C***H***$_2$SO$_3$), 2.50 (s, 2H, -C***H***$_2$S), 1.96-1.94 (d, 2H, *J* = 6.65 Hz, -C***H***$_2$CH_2S). ^{13}C-NMR (100.6 MHz, dmso-d_6): $^{\delta}$ 135.8 (***C***1-Ar), 132.3 (***C***2 & ***C***6-Ar), 132.2 (***C***3 & ***C***5-Ar), 121.6 (***C***4-Ar), 50.7 (-***C***H$_2$SO$_3$), 40.2 (Ar-***C***H$_2$S), 36.6 (-**C**H$_2$S), 24.9 (-***C***H$_2$CH_2S). IR (KBr) (wavenumber, cm^{-1}): 3513, 2931 (C-Cs), 1627, 1486, 1287, 1173, 1064 (C=S), 817 (C-Cb). Elemental Analysis, Calcd for $C_{11}H_{13}BrO_3S_4$: C) 31.21%, H) 2.86%. Found: C) 31.28%, H) 3.17%.

3-(4-methoxy-benzylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid sodium salt[26]

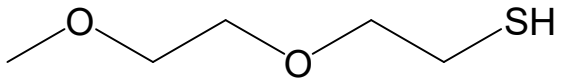


3j

(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%), ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 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), ^{13}C-NMR (400 MHz, dmso-d_6): δ 224.2, 159.2, 130,9, 127.0, 114.4, 55.5, 50.3, 40.5, 35.9, 24.6.

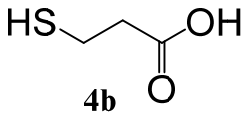
bis[2-(2-methoxyethoxy)-ethanethiol[27] (4a): To a 6.45 mL (1.0 g, 3.6 mmol) in *situ* solution of



4a

in 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was added 1-bromo-2-(2-methoxyethoxy)-ethane, (0.66 g, 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 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 $MgSO_4$ and filter. The filtrate was concentrated to give thiol as residual oil. (640 mg, 65%). ^{1}H-NMR (400 MHz, $cdcl_3$): δ 3.63.-3.60 (t, 4H, *J* = 6.1 Hz, CH_3O-C***H***$_2$-C***H***$_2$O-), 3.56-3.54 (t, 2H, *J* = 4.5 Hz, -OC***H***$_2CH_2S$), 3.38 (s, 3H, -OC***H***$_3$), 2.73-2.68 (m, 2H, -C***H***$_2$S), 1.61-1.57 (t, 1H, SH, *J* = 8.2 Hz, -CH_2S). ^{13}C-NMR (100.6 MHz, $cdcl_3$): δ 71.3 (CH_3O-***C***H_2-CH_2O-), 70.6 (CH_3O-CH_2-***C***H_2O-), 69.8 (-O***C***H_2CH_2S), 58.4 (-O***C***H_3), 29.7 (-**C**H_2S). IR (KBr) (wavenumber, cm^{-1}): 2877 (C-Cs), 1454, 1355, 1293, 1198, 1140 (C=S), 735 (C-Cb). Elemental Analysis, Calcd for $C_5H_{12}O_2S$: C) 44.09%, H) 8.88%. Found: C) 44.01%, H) 9.19%.

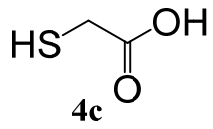
3-Mercaptopropanoic acid[28] (4b): In the manner described above, To a 6.45 mL (1.0 g, 3.6 mmol) in *situ* solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was treated 3-bromopropanoicacid, (0.55 g, 3.6 mmol) in presence catalytic amount of tetrabutylammonium bromide (20 mg) to obtain product as residual oil (296 mg, 77.8%). ^{1}H- NMR (400 MHz, $CDCl_3$): δ 11.67 (br-s, 1H, COOH), 2.77-267 (m, 4H, HSC***H***$_2$C***H***$_2$), 1.69-1.67 (t, *J* = 7.8 Hz, SH). NMR (400 MHz, d_2o): δ



4b

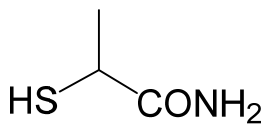
2.657-261 (m, 4H, HSC***H*****2**C***H*****2**), ^{13}C-NMR (100.6 MHz, $CDCl_3$): $^{\delta}$ 178.0 (***C***OOH), 38.1 (HS**C**H_2CH_2), 19.1 (HOOC**C**H_2CH_2). ^{13}C-NMR (100.6 MHz, d_{2O}):): $^{\delta}$ 178.6 (***C***OOH), 38.2 (HS**C**H_2CH_2), 19.3 HOOC***C***H_2CH_2).

2-Mercaptoacetic acid[29] (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%). ^{1}H-NMR (400 MHz, $CDCl_3$): $^{\delta}$ 3.06 (s, 2H, HSC***H*****2**COOH), ^{13}C-NMR (100.6 MHz, d_{2O}): $^{\delta}$ 178.6 (*C*OOH), 29.0 (HSCH_2COOH),



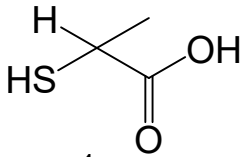
4c

2-Mercapto-2-methyl-propanamide[30] (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%). ^{1}H-NMR (400 MHz, d_{2O}): $^{\delta}$ 3.76-3.71 (m, 1H, -C***H***CH_3), 1.46-1.51 (m, 3H, -CHC***H*****3**). ^{13}C-NMR (100.6 MHz, d_{2O}):): $^{\delta}$ 178.2 (***C***ONH_2), 42.9 (-***C***HCH_3), 17.6 (-CH***C***H_3).



4d

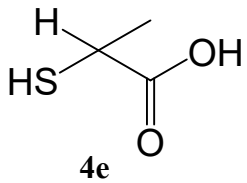
2-Mercapto-propanoic acid[31] (4e): To a 6.45 mL (1.0 g, 3.6 mmol) situ solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonicacid disodium salt was added 2-bromopropanoicacid, (560 mg, 3.6 mmol) in presence of catalytic amount of tetra butyl ammonium bromide (20 mg). Stir the reaction mixture for 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



4e

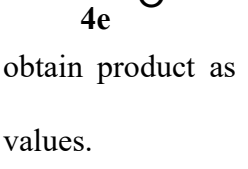
(100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to give product as residual oil (280 mg, 73%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.14 (br-s, 1H, COOH), 3.58-3.50 (m, 1H, HSC***H***CH_3), 2.25-2.23 (s, *J* = 7.8 Hz, 1H, -SH) 1.55-1.53 (d, *J* = 7.8 Hz, HOOCCHC***H***$_3$). ^{13}C-NMR (100.6 MHz, d_2O): δ 180.0 (***C***OOH), 35.5 (HS**C**HCH_3), 20.6 (HOOCCH**C**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.



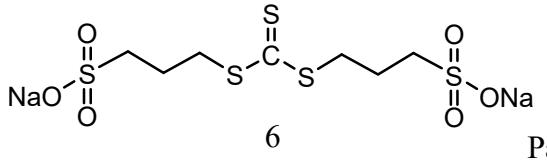
4e

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 194-196ºC. ^{1}H-NMR (400 MHz, dmso-d_6): δ 12.74 (br-s, 1H, COOH), 3.45 (s, 1H, HS), 1.44 (s, 6H, HSC(C***H***$_3$)$_2$) ^{13}C-NMR (100.6 MHz, d_2O): δ 180.0 (***C***OOH), 57.5 (HS**C**HCH_3), 30.7 (HOOCC**C**H_3)$_2$). IR (KBr) (wavenumber, cm^{-1}): 298010, 2654 (C-Cs), 1688, 1464, 1289, 1165, 1113 (C=S), 809 (C-Cb).



4g

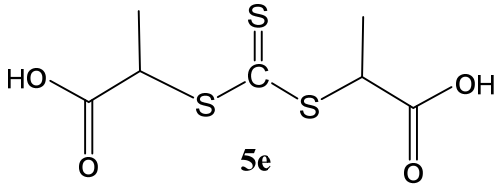
3-(3-Sulfo-propylsulfanylthiocarbonylsulfanyl)-propane-1-sulfonic acid, di sodium salt (6): To a 6.45 mL (1.0 g, 3.6 mmol) *in situ* solution of in 3-dithiocarboxysulfanyl-propane-1-sulfonicacid



6

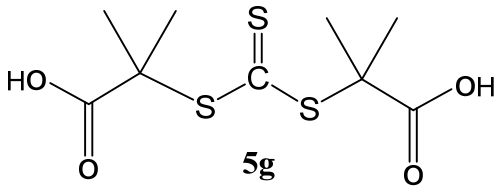
disodium salt was added 2-bromo propanoic acid, (430 mg, 3.6 mmol). Stir the reaction mixture for overnight (12 h), during reaction time yellow solid is formed. Filter the yellow solid, suspended in acetone, filter and dry in vacuum to give compound **6** (550 mg, 44.1%). Mp >250ºC. ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 3.50-3.47 (t, 4H, *J* = 6.8 Hz, -*CH*$_2$SO$_3$), 2.55-2.51 (t, 4H, *J* = 7.2 Hz, -*CH*$_2$S), 1.96-1.93 (t, 4H, *J* = 7.0 Hz, -C*H*$_2$*C*H$_2$S). ^{13}C-NMR (100.6 MHz, dmso-d_6): $^{\delta}$ 50.6 (-***C***H$_2$SO$_3$), 36.2 (-***C***H$_2$S), 24.9 (-***C***H$_2$*C*H$_2$S). ^{1}H-NMR (400 MHz, d_2o): $^{\delta}$ 3.50-3.47 (t, 2H, *J* = 7.2 Hz, -*CH*$_2$SO$_3$), 2.96-2.92 (t, 2H, *J* = 7.2 Hz, -*CH*$_2$S), 2.13-2.05 (m, 2H, -C*H*$_2$*C*H$_2$S). ^{13}C-NMR (100.6 MHz, d_2o): $^{\delta}$ 50.0 (-***C***H$_2$SO$_3$), 35.2 (-***C***H$_2$S), 23.6 (-***C***H$_2$*C*H$_2$S). IR (KBr) (wavenumber, cm^{-1}): 3510, 2931 (C-Cs), 1626, 1418, 1216, 1172, 1049 (C=S), 828 (C-Cb). Elemental Analysis, Calcd for $C_7H_{12}BrNa_2O_6S_5$: C) 21.10%, H) 3.05%. Found: C) 21.14%, H) 3.70%. Single crystal data confirmed the structure.

2-mercapto propanoic acid trithiocarbonate[33] (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.



5e

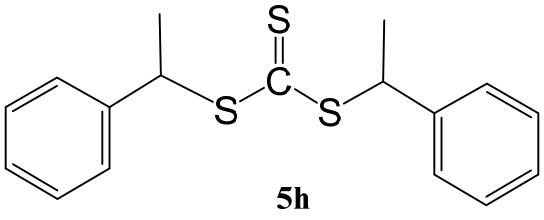
2,2'-[(Thioxomethylene)disulfanyl]bis(2-methylpropanoic acid)[7] (5g): In the manner described above, 2.5 g (14 mmol) of 3-mercapto-1-propane-sulfonicacid sodium salt was treated with sodium hydroxide (1.68 g, 42 mmol), carbon disulfide (1.06 g, 0.84 mL, 14 mmol) followed by 2-bromo-2-methyl-propanoic 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



5g

vacuum to give trithiocarbonate **5g** (1.22 g, 62%). Mp =186.59ºC. ^{1}H-NMR (400 MHz, dmso-d_6): $^{\delta}$ 1.58 (s, 12H, S-C(C***H***$_3$)$_2$-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(***C***H$_3$)$_2$-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 $C_9H_{14}O_4S_3$: C) 38.28%, H) 5.00%. Found: C) 38.71%, H) 5.04%.

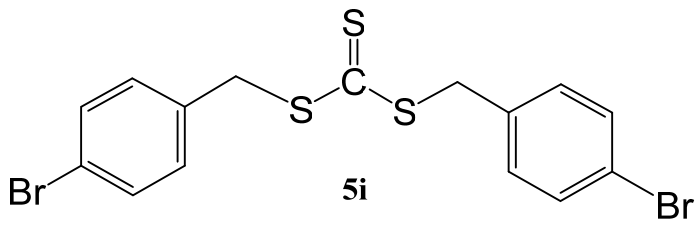
Carbonotrithioic acid, bis(1-phenylethyl) ester[34] (5h): In the manner described above, to a



5h

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 -SC***H***(CH$_3$), 1.73-1.54 (m, 3H, (S-C(C***H***$_3$) ^{13}C-NMR (100.6 MHz, $CDCl_3$): $^{\delta}$ 140.9, 128.5, 127.6, 127.6, 49.9 (S-***CH***(CH$_3$), 21.5 (S-C(***C***H$_3$).

Carbonotrithioic acid, bis[(4-bromophenyl) methyl] ester[35] (5i): In the manner described

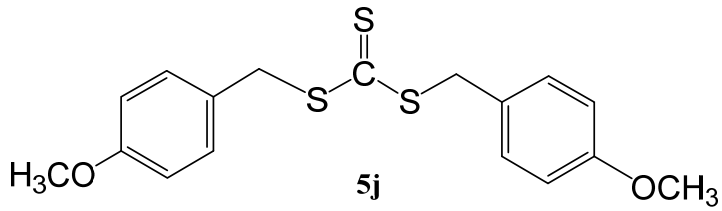


5i

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

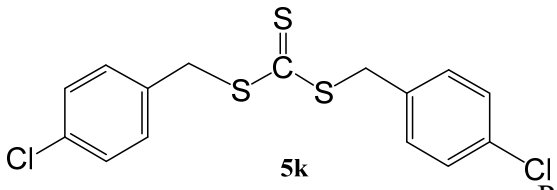
remove solid **6** and extracted the aqueous layer with ether (50 mL x 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated gives trithiocarbonate **5i** (560mg, 70%). Mp = 93.27°C. The compounds **5i** is confirmed by single crystals data. ^{1}H-NMR (400 MHz, $CDCl_3$): $^{\delta}$ 7.44 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.54 (s, 2H, -SC***H***Ph). ^{13}C-NMR (100.6 MHz, $CDCl_3$): $^{\delta}$ 134.0, 131.7, 130.6, 121.7, 40.6 (S-***C***HPh). 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[36] (5j): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid 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%). ^{1}H-NMR (400 MHz, $CDCl_3$): $^{\delta}$ 7.26 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.57 (s, 2H, -SC***H***Ph), 3.80 (s, 3H, ($PhOCH_3$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): $^{\delta}$ 223.1 (C=S), 159.1, 130.5, 126.6, 114.1, 55.2, 41.1.



5j

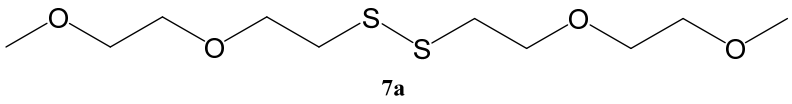
Carbonotrithioic acid, bis[(4-chlorophenyl) methyl] ester[37] (5k): In the manner described above, to a 6.45 mL (1.0 g, 3.6 mmol) situ solution of 3-dithiocarboxysulfanyl-propane-1-sulfonicacid



5k

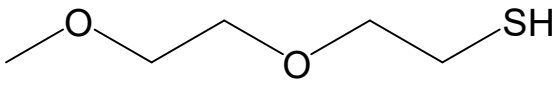
disodium salt was treated 4-chlorobenzylchloride (577 mg, 3.6 mmol). After the completion of reaction (12 h), filtered to remove solid **6** and extracted the aqueous layer with ether (50 mL x 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated gives trithiocarbonate **5k** (515 g, 80%). Melting point is 55-57ºC ^{1}H-NMR (400 MHz, cdcl$_3$): $^{\delta}$ 7.25 (s, 4H), 4.55 (s, 2H). ^{13}C-NMR (400 MHz, cdcl$_3$): $^{\delta}$ 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 80ºC 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 MgSO$_4$ and filter. The filtrate was concentrated to obtain disulfide **7a** as residual oil (202 mg, 42 %). ^{1}H-NMR (400 MHz, cdcl$_3$): $^{\delta}$ 3.74-3.61 (m, 8H, CH$_3$O-C***H***$_2$-C***H***$_2$O-), 3.55-3.53 (dd, 4H, J = 2.5 Hz and 3.8 Hz, -OC***H***$_2$CH$_2$S), 3.38 (s, 6H, -OC***H***$_3$), 2.78-2.75 (t, 4H, J = 6.9 Hz, -C***H***$_2$S). ^{13}C-NMR (100.6 MHz, cdcl$_3$): $^{\delta}$ 71.8 (CH$_3$O-***C***H$_2$-CH$_2$O-), 71.0 (CH$_3$O-CH$_2$-***C***H$_2$O-), 70.2 (-O***C***H$_2$CH$_2$S), 59.7 (-O***C***H$_3$), 31.7 (-**C**H$_2$S). IR (KBr) (wavenumber, cm^{-1}): 2876 (C-Cs), 1354, 1275, 1198, 1100 (C=S), 733 (C-Cb). Elemental Analysis, Calcd for C$_{10}$H$_{22}$O$_4$S$_2$: C) 44.42%, H) 8.20%. Found: C) 44.29%, H) 8.19%.



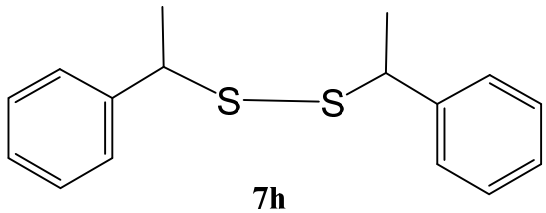
7a

bis[2-(2-methoxyethoxy)-ethanethiol[27] (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 $MgSO_4$ and filter. The filtrate was concentrated to give thiol **4a** as residual oil. (216 mg, 44%).



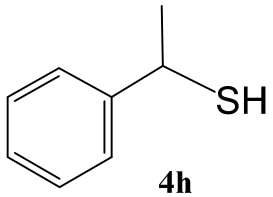
4a

bis(1-phenylethyl) disulfide[38] (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 80ºC 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.



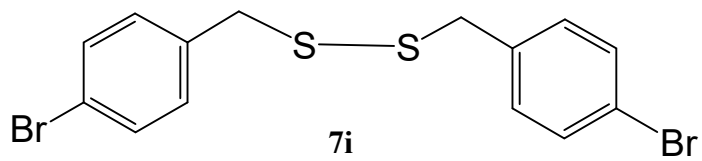
7h

1-phenylethyl thiol[39] (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 $MgSO_4$ and filter. The filtrate was concentrated to give thiol **4i** as residual oil. (170 mg, 36%). NMR data is consistent with reported values.



4h

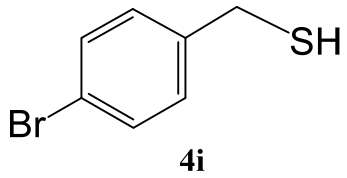
Bis(p-bromobenzyl) disulfide[40] (7i): To a 6.45 mL (1.0 g, 3.6 mmol) in *situ* solution of **6**, was added 4-bromobenzylbromide (0.9 g, 3.6 mmol) and heat at 80ºC for 2 h. The reaction mixture was dilute with water



7i

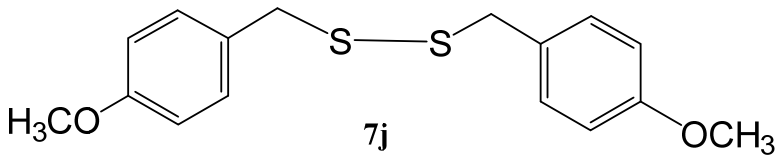
and extract with ether (25 mL X 2), and the organic layer was washed with water (100 mL), brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated give disulfide **7i** (138 mg, 38%). NMR data is consistent with reported values.

p-bromobenzyl thiol[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 $MgSO_4$ and filter. The filtrate was concentrated to give thiol **4i** as residual oil. (290 mg, 40%). NMR data is consistent with reported values.



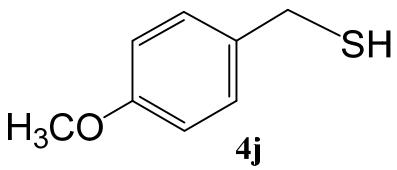
4i

Bis(p-methoxybenzyl) disulfide[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°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.



7j

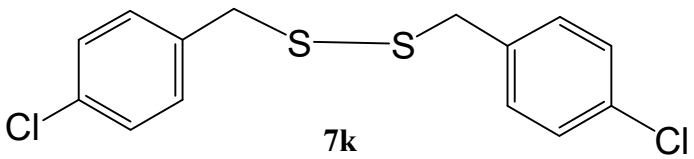
p-methoxybenzyl thiol[43] (4j): The aqueous layer on acidified with concentrated HCl to pH=2, then extract with ether (25 mL X 2), wash the ether layer with water (50 mL), brine solution (50 mL), dried over $MgSO_4$ and filter. The filtrate was concentrated to give thiol **4i** as residual



4j

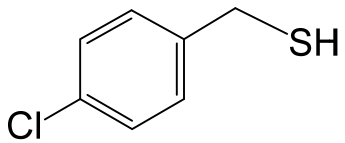
oil. (210 mg, 38%). NMR data is consistent with reported values.

Bis(p-chlorobenzyl) disulfide[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°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.



7k

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).



4k

Reference:

1. Hawker, C. J.; Bosman, A. W.; Harth, E., New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations. *Chem. Rev. (Washington, D. C.)* **2001,** *101* (12), 3661-3688.
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