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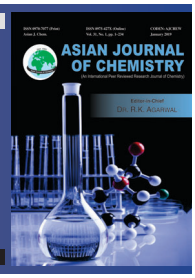

Triton B Mediated One-Pot Synthesis of Thiocarbonic Ester Derivatives in Non-Aqueous Medium

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A differentiated series of thiocarbonic acid esters have been synthesized and characterized in good to excellent yields with the help of thiols, carbon di sulphide and alkyl/aryl halides in DMSO with benzyl trimethylammonium hydroxide where Triton B acts as a catalyst. This method is safer and efficient as compared to other conventional methods.

Keywords: Thiocarbonic acid, Thiocarbonic acid esters, Thiols, Triton B.

INTRODUCTION

Trithiocarbonic acids and their derivative esters comprise of vital class of compounds for various industrial, synthetic and medicinal applications.They are extensively used in various aspects as additives, lubricating oils [1-3], pesticides, vulcanization promoters, stabilizers and polymeric composition additives [4]. Their derivatives are used in reversible and addition fragmentation in chain transfer [5]. They have been popularly used as pesticides, insectides [2], protective group [3], pharmaceuticals [5-19], medicinal chemistry [5,20-23] and as a active linkers in organic synthesis [24,25]. Some of the conventional methods was used for the synthesis of thiocarbonic acid esters with thiophosgene [26], chlorodithioformate [4] and their derivatives with carbon monoxide [21]. However, several problems persist as high reaction temperatures, longer reaction time and tedious purification problems, use of enormous amount of catalyst with lesser yields so different metal catalysts have been employed for high yield product formation [22]. There are other methods too like reaction of aryl chloroformate with alkane thiols [23], benzene thiols and alkyl halides with carbon disulfide in presence of phase transfer catalyst [24,25], dialkylation of the trithiocarbonate anion with halide using phase transfer catalyst [26] or sodium trithiocarbonates with alkyl halides [4]. However, these methods require complex starting materials which are mostly expensive, require high temperatures [27-30]. Also, formation of undesired side products has been reported. Thus there remain still the need to develop better methods by searching novel reagents and catalytic system.

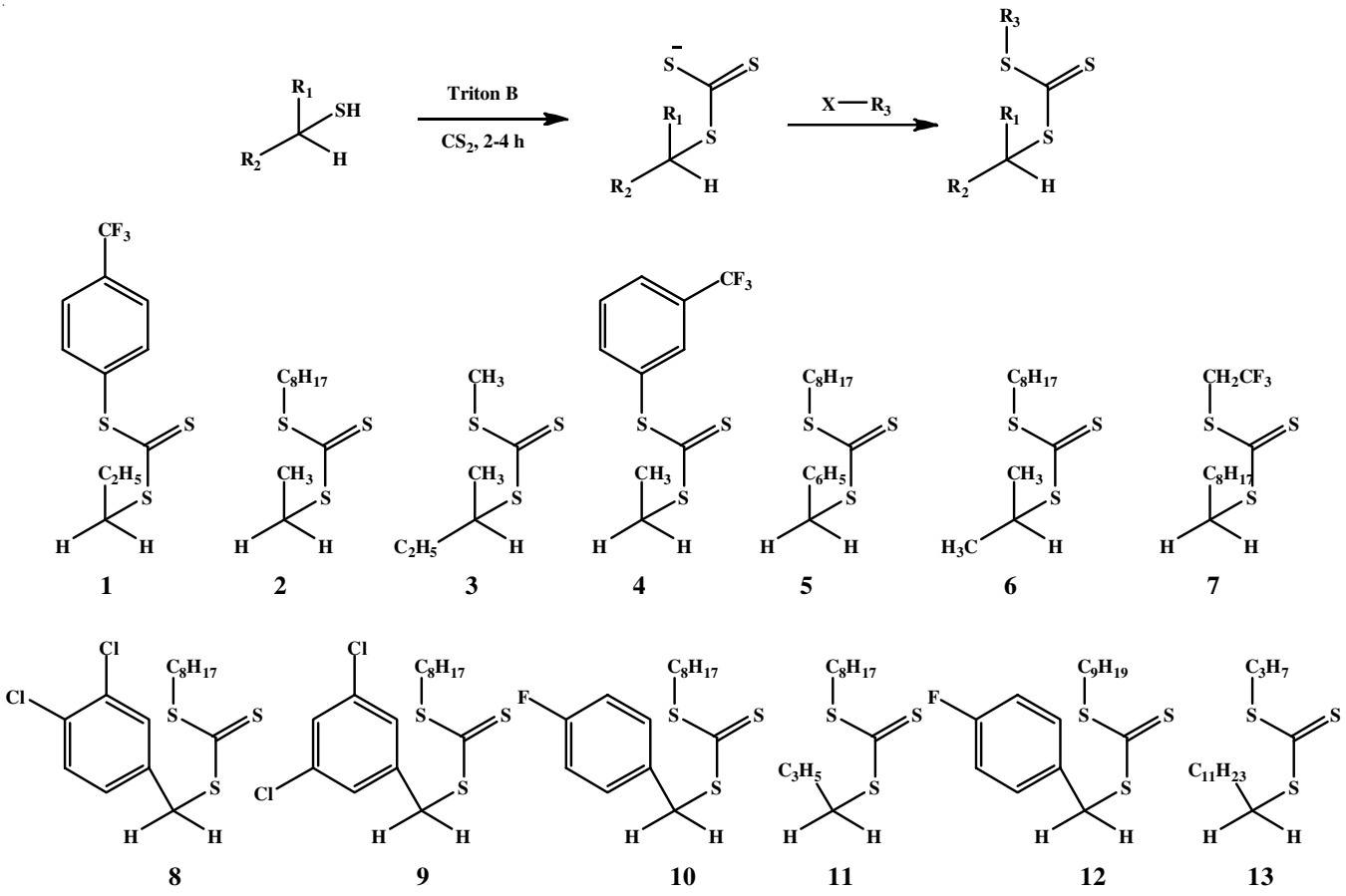
Present work is focussed on development of novel and efficient synthetic methodologies for synthesis of cyclic and acyclic trithiocarbonic acid esters through *in situ* employment of CS_2 from corresponding thiols deploying a phase transfer catalyst, benzyl trimethylammonium hydroxide. Thus, we report highly efficient, chemoselective, mild synthesis of trithiocarbonic acid esters of primary, secondary, tertiary thiols using benzyl trimethylammonium hydroxide.

The synthesis of trithiocarbonic acid esters is carried out by mild thiocarbonation of thiols with carbon disulphide mediated by benzyl trimethylammonium hydroxide at room temperature.

EXPERIMENTAL

All the chemicals and solvents were produced by Merck, Sigma-Aldrich and Fluka chemical. Reactions were carried out under an atmosphere of nitrogen atmosphere. NMR spectra were obtained on an AC-300F instrument ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) using $CDCl_3$ solvents and TMS as an internal standard. Mass spectra were recorded using a Bruker Esquire 3000 spectrometer.

Synthesis: To a solution of thiols (1 mmol) in DMSO, added carbon disulphide under nitrogen atmosphere and stirred for 15 min to generate the intermediate. Further added Triton-B and alkyl halides after reaction mixture were stirred for 2 h to afford trithiocarbonic acid esters (**Scheme-I**). Alkyl halides



Scheme-I: Synthesis of trithiocarbonic acid derivatives from thio alcohols and alkyl/aryl halide derivatives

and thiols are taken in the 1:1 ratio. After completion of reaction, the reaction mixture was extracted with ethyl acetate to yield trithiocarbonic acid esters upto 94-99 %.

Trithiocarbonic acid propyl ester 3-trifluoromethylphenyl ester (1): Yellow oily liquid; yield: 94 %; b.p.: 440-445 ºC. ^{1}H NMR ($CDCl_3$): δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.13(s, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 2.91 (t, *J* = 7.2 Hz, 2H), 1.77-1.64 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 293.27[M^+]. Anal. calcd. found (%) $C_{11}H_{11}S_3F_3$: C 44.57 (44.80); H, 3.74 (3.69); S, 32.45 (32.42); F, 19.23 (19.25).

Trithiocarbonic acid ethyl ester octyl ester (2): Yellow oily liquid; yield: 97 %; b.p.: 415-418 ºC. ^{1}H NMR ($CDCl_3$): δ 3.38 (d, *J* = 4.8 Hz, 2H), 3.34 (d, *J* = 6.8 Hz, 2H), 1.73-1.65 (m, 2H), 1.41-1.38 (m, 2H), 1.37-1.33 (m, 3H), 1.31-1.27 (m, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 250.9 [M^+]. Anal. calcd. found (%) $C_{11}H_{22}S_3$: C, 52.74 (52.78); H, 8.85 (8.80); S, 38.40 (38.46).

Trithiocarbonic acid *sec*-butyl ester methyl ester (3): Yellow oily liquid; yield: 94 %; b.p.: 300-303 ºC. ^{1}H NMR ($CDCl_3$): δ 4.15-4.09 (m, 1H), 2.73 (s, 3H), 1.81-1.65 (m, 2H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 180.06 [M^+]. Anal. calcd. found (%) $C_6H_{12}S_3$: C, 39.96 (39.91); H, 6.71 (6.68); S, 53.34 (53.39).

Trithiocarbonic acid ethyl ester 3-trifluoromethylphenyl ester (4): Yellow oily liquid; yield: 97 %. ^{1}H NMR ($CDCl_3$): δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 6.99 (d, *J* = 6.8 Hz, 1H), 2.96 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 279.3[M^+]. Anal. calcd. found (%) $C_{10}H_9S_3F_3$: C, 42.54 (42.57); H, 3.21 (3.18); S, 34.07 (34.02); F, 20.18 (20.15).

2-Phenyl trithiocarbonic acid ethyl ester octyl ester (5): Yellow oily liquid; yield: 95 %; ^{1}H NMR ($CDCl_3$): δ 7.35-7.26 (m, 4H), 4.61 (s, 1H), 3.35 (t, *J* = 3.46 Hz, 2H), 1.72-1.66 (m, 2H), 1.41-1.27 (m, 11 H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.19, 129.24, 128.67, 128.46, 127.70, 43.76, 41.34, 38.72, 31.78, 29.08, 28.90, 28.47, 28.01, 27.97, 22.61, 14.06. MS (ESI) (*m/z*): 329.92 [M^++1]. Anal. calcd. found (%) $C_{17}H_{28}S_3$: C, 62.14 (62.11); H, 8.59 (8.52); S, 29.27 (29.29).

Trithiocarbonic acid isopropyl ester octyl ester (6): Yellow oily liquid; yield: 94 %; b.p.: 437-440 ºC. ^{1}H NMR ($CDCl_3$): δ 4.24-4.16 (m, 1H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.2 Hz, 2H), 1.72-1.54 (m, 4H), 1.41-1.39 (m, 12H), 0.87 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 264.2 [M^+]. Anal. calcd. found (%) $C_{12}H_{24}S_3$: C, 54.49 (54.43); H, 9.15 (9.17); S, 36.37 (36.33).

Trithiocarbonic acid octyl ester 2,2,2-trifluoroethyl ester (7): Yellow oily liquid; yield: 97 %; b.p.: 410-412 ºC. ^{1}H NMR ($CDCl_3$): δ 2.52 (q, *J* = 7.2 Hz, 2H), 1.61 (q, *J* = 7.6 Hz, 2H), 1.40-1.27 (m, 12 H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 302.1 [M^+]. Anal. calcd. found (%) $C_{11}H_{19}S_3F_3$: C, 43.39 (43.35); H, 6.29 (6.27); S, 31.60 (31.58); F, 18.72 (18.70).

Trithiocarbonic acid 3,4-dichloro ester octyl ester (8): Yellow oily liquid; yield: 94 %; ^{1}H NMR ($CDCl_3$): δ 7.49- 7.42 (m, 1H), 7.39-7.36 (m, 1H), 7.23-7.16 (m, 1H), 4.54 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 2H), 1.70 (q, *J* = 7.6 Hz, 2H), 1.41-1.27 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 381. Anal.

calcd. found (%) $C_{16}H_{22}S_3Cl_2$: C, 50.38 (50.35); H, 5.81 (5.78); S, 25.22 (25.26); Cl, 18.59 (18.52).

Trithiocarbonic acid 3,5-dichlorobenzyl ester octyl ester (9): Yellow oily liquid; yield: 96%; b.p.: 560-564 ºC. ^{1}H NMR ($CDCl_3$): δ 7.32-7.25 (m, 1H), 7.25-7.22 (m, 2H), 4.54 (s, 2H), 3.374 (q, *J* = 7.6 Hz, 2H), 1.73-1.66 (m, 2H), 1.41-1.27 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). MS (ESI) (*m/z*): 382. Anal. calcd. found (%) $C_{16}H_{22}S_3Cl_2$: C, 50.38 (50.36); H, 5.81 (5.83); S, 25.22 (25.19); Cl, 18.59 (18.56).

Trithiocarbonic acid 4-fluorobenzyl ester octyl ester (10): Yellow oily liquid; yield: 95 %; b.p.: 583-586 ºC. ^{1}H NMR ($CDCl_3$): δ 7.59-7.55 (m, 2H), 7.46-7.43 (m, 2H), 4.66 (s, 2H), 3.37 (t, *J* = 8.0 Hz, 2H), 1.73-1.60 (m, 2H), 1.40-1.27 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 163.46, 131.37, 130.89, 130.81, 130.63, 115.61, 115.40, 40.38, 37.97, 31.73, 29.03, 28.88, 28.00, 27.94, 22.60. MS (ESI) (*m/z*): 329.92 [M^+]. Anal. calcd. found (%) $C_{16}H_{23}S_3F$: C, 58.14 (58.11); H, 7.01 (7.08); S, 29.10 (29.13); F, 5.75 (5.71).

Trithiocarbonic acid but-3-enyl ester octyl ester (11): Yellow oily liquid; yield: 93 %; b.p.: 457-460 ºC. ^{1}H NMR ($CDCl_3$): δ 5.85-5.78 (m, 1H), 5.14-5.06 (m, 2H), 3.41 (t, *J* = 7.2 Hz, 2H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.54-2.44 (m, 2H), 1.65-1.54 (m, 2H), 1.39-1.27 (m, 10H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.66, 116.78, 36.91, 35.84, 34.004, 32.13, 31.78, 29.16, 29.08, 29.03, 28.84, 28.37, 27.98. MS (ESI) (*m/z*): 277.19 [M^++1]. Anal. calcd. found (%) $C_{13}H_{24}S_3$: C, 56.46 (56.42); H, 8.75 (8.71); S, 34.79 (34.81).

Trithiocarbonic acid 4-fluorobenzyl ester nonyl ester (12): Yellow oily liquid; yield: 94 %; b.p.: 583-587 ºC. ^{1}H NMR ($CDCl_3$): δ 7.32-7.28 (m, 2H), 7.01-6.97 (m, 2H), 4.58 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 2H), 1.73-1.66 (m, 2H), 1.41-1.27 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (ESI) (*m/z*): 344.25 [M^++1]. Anal. calcd. found (%) $C_{17}H_{25}S_3F$: C, 59.26 (59.22); H, 7.31 (7.31); S, 27.92 (27.86); F, 5.51 (5.55).

Trithiocarbonic acid dodecyl ester propyl ester (13): Yellow oily liquid; yield: 98 %; b.p.: 529-533 ºC. ^{1}H NMR ($CDCl_3$): δ 3.35 (t, *J* = 7.2 Hz, 4H), 1.72-1.55 (m, 4H), 1.41-1.25 (m, 18H), 0.87 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 31.90, 31.76, 29.61, 29.54, 29.43, 29.33, 29.17, 29.10, 29.07, 29.03, 28.91, 28.38, 28.0003, 22.68, 22.62, 14.11. MS (ESI) (*m/z*): 320 [M^+]. Anal. calcd. found (%) $C_{16}H_{32}S_3$: C, 59.94 (59.96); H, 10.06 (H, 10.02); S, 30.00 (30.03).

RESULTS AND DISCUSSION

Several solvents like dimethyl sulphoxide, N, N-dimethyl formamide, benzene, acetonitrile, dichloromethane, hexane, heptanes, methanol, chloroform and acetone were investigated and found that DMSO proved to be the most suitable solvent for carrying out the transformation.

A comparative study of use of various mild bases in caring out this synthetic reaction was studied where it was further realized that best yields were obtained using Triton-B. The synthesis of trithiocarbonic acid esters was adopted by reacting thiols with primary, secondary and tertiary alkyl/aryl halides in DMSO in CS_2 environment in presence of Triton-B, a phase transfer catalyst at room temperature for 2-4 h to afford trithiocarbonic acid esters in a very good to excellent yields (94-99 %) (Table-1).

TABLE-1
CONVERSATION OF THIOLS INTO TRITHIOCARBONIC ACID ESTERS

Entry	R_1	R_2	R_3	Time (h)	Yield (%)
1	C_2H_5	H	$C_7H_4F_3$	2.0	94
2	CH_3	H	C_8H17	2.0	97
3	C_2H_5	CH_3	CH_3	2.5	94
4	CH_3	H	$C_7H_4F_3$	2.0	97
5	C_6H_5	H	C_8H_{17}	2.5	95
6	CH_3	CH_3	C_8H_{17}	2.0	94
7	C_8H_{17}	H	CH_4CF_3	2.5	97
8	$C_6H_3Cl_2$	H	C_8H_{17}	2.5	96
9	$C_6H_3Cl_2$	H	C_8H_{17}	2.5	95
10	C_6H_4F	H	C_8H_{17}	2.0	93
11	C_3H_5	H	C_8H_{17}	2.0	94
12	C_6H_4F	H	C_9H_{19}	2.0	97
13	$C_{11}H_{23}$	H	C_3H_7	2.5	98

The novel one pot synthesis yields good to excellent amount of trithiocarbonic acid esters, both cyclic and acyclic substituent at room temperature. The method deals with the short comings and provides safer reaction conditions, simple work ups, faster reaction times and high yields.

Conclusion

A convenient and efficient protocol for the one pot, three components coupling of a range of primary, secondary and tertiary range thiols and alkyl/aryl halides *via* combination of Triton B and carbon disulphide is developed. This reaction generates corresponding thiocarbonic acid esters in excellent yields (94-99 %) at the room temperature. Furthermore, this method offers substrate versatility, mild reaction conditions and experimental convenience. This synthetic protocol is believed to offer a more general method for the formation of carbon to sulphur bonds essential to numerous organic syntheses.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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