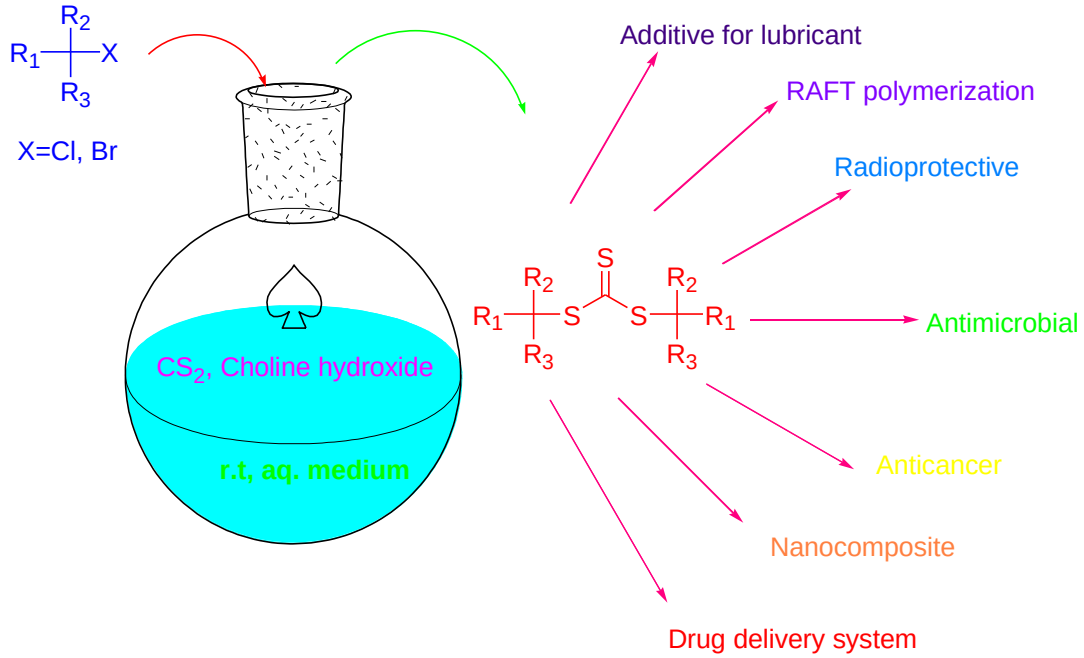
CHOLINE HYDROXIDE MEDIATED NOVEL, CLEANER, GREENER SYNTHESIS OF SYMMETRICAL TRITHIOCARBONATES

Km. Divya[1*], Amit K Chaturvedi[2*], Nitin Srivastava[3*]

Abstract

A cleaner, greener, and effective synthesis for the symmetric trithiocarbonates is being reported using minimum amount of biodegradable water-soluble organic base choline hydroxide, carbon disulfide and alkyl halides. Choline hydroxide acts as a strong organic base to carry out the formation of trithiocarbonates anion. It also acts as phase transfer catalyst to make interaction among the reagents better and give higher yield in less time. So, the reported method is a step towards sustainable and green chemistry.

Graphical Abstract



Keywords: Trithiocarbonates, carbon disulfide, choline hydroxide, green synthesis

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1. Introduction

Inclusion of sulfur bond is one of the prominent tasks undertaken by researchers[1]. Trithiocarbonates are such very important class of compounds having diversified applications including agriculture[2-4], additives for lubricants[5-7]. Organic trithiocarbonates have been efficiently employed as reversible addition fragmentation chain transfer (RAFT)[8-12] agent, in organic synthesis, industrial processes and drug synthesis[13]. They have been reported as Radioprotective[14], antimicrobial[15], anticancer[16], nano composite[17], controlled drug delivery[18], drug delivery[19]. Such diversified applications of trithiocarbonates, demand a cheaper, easier, and eco-friendly synthesis of trithiocarbonates.

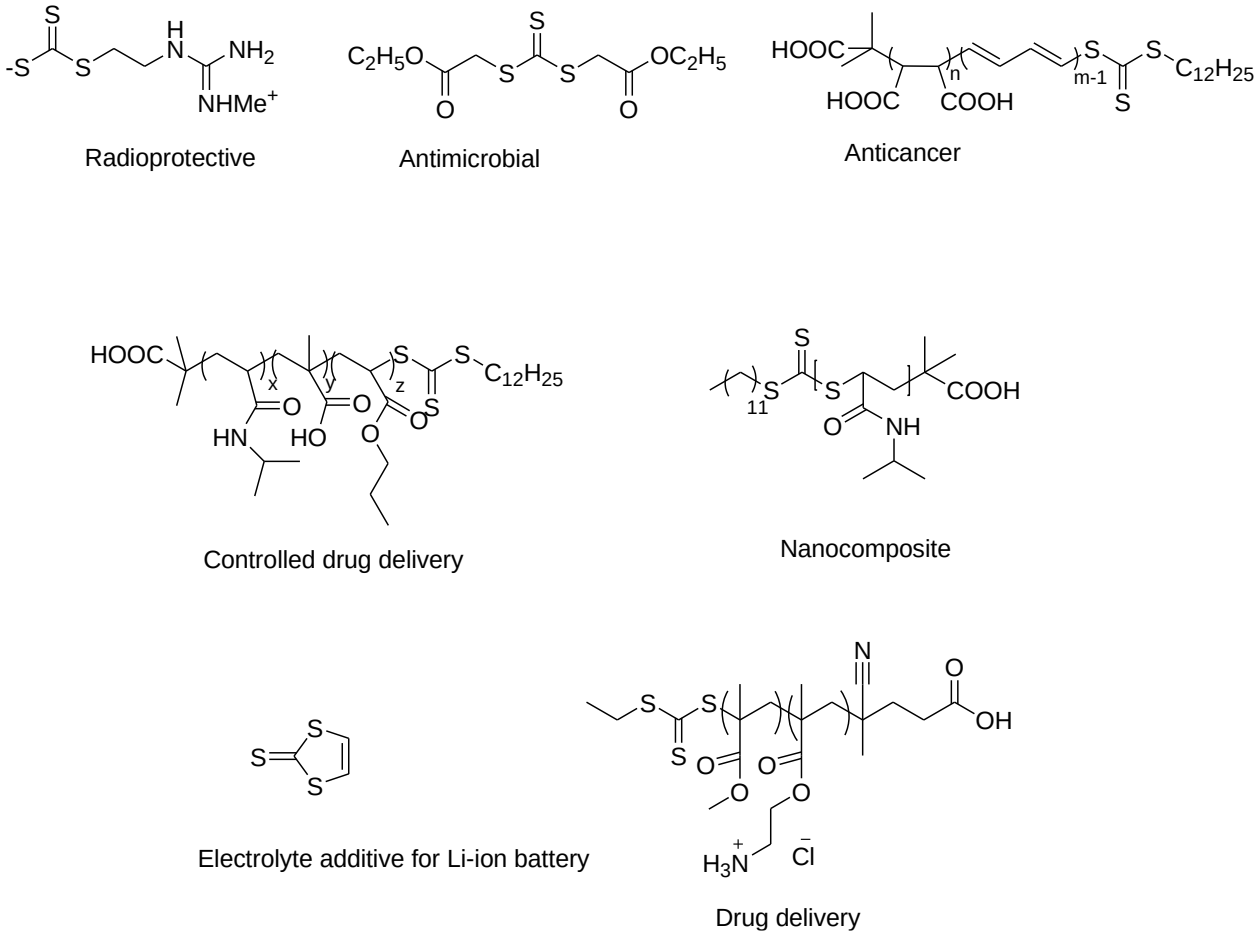


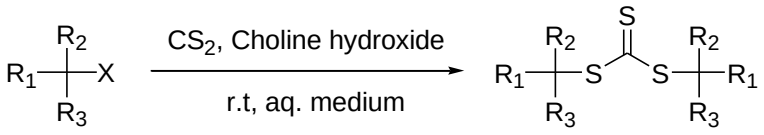
Fig 1. Structurally diverse biologically potent trithiocarbonates

Earlier synthesis of trithiocarbonates makes use of reactions between thiols and thiophosgene[20] or chlorodithioformates[21], and in other ways reaction of thiols and CS_2 and later with alkyl halides in basic medium[22]. Such synthesis however, employed toxic reagents with harmful odors. The other process for the formation of symmetrical trithiocarbonates is employing alkyl halides to alkylatethrithiocarbonate anion in the presence of phase transfer catalysis or high temperature. The process of alkylation is also not easy and requires high amount of CS_2 and bases like NaOH[23], KOH[24], NH_4OH[25], Al_2O_3[26], CS_2CO_3[27,36,37], KF/Al_2O_3[28], N-Bu_4NOH[29], K_3PO_4[30], $KOH/TBAB/Al_2O_3$[31], K_2CO_3[32], NH4OAc[33], metal sulfides[34], tetraethylene glycol complex[35], ion exchange resin[38] which are big sources of the environmental pollution and are constraint to the sustainable development. So, there is need of a process which consume minimum amount of carbon disulfide and biodegradable base to achieve cleaner greener and efficient synthetic route. The communicated research envisages an efficient and new one pot method for synthesizing the symmetric trithiocarbonates using several alkyl halides and minimum amount of biodegradable water-soluble organic base choline hydroxide and CS_2. Choline hydroxide acts as a strong organic base to carry out the formation of trithiocarbonates anion. It also acts as phase transfer catalyst to make interaction among the reagents better and give higher yield in less time.

2. Results and Discussion

The representative reaction between benzyl chloride, CS_2, was carried out in aqueous medium in the presence of the phase transfer organic catalyst choline hydroxide at room temperature

(Scheme 1)



X=Cl, Br

Scheme 1 Synthesis of symmetrical trithiocarbonates employing choline hydroxide

The product dibenzyl trithiocarbonates was a pale-yellow oil which was characterized with the help of IR, NMR and elemental analysis. It was found that the IR showed a stretching frequency of 1065 cm^{-1} which corresponds to C=S confirming the formation of the trithiocarbonates bond. The NMR spectra of the synthesized compound showed peaks at δ 4.68 and 7.30-7.40 corresponding to (4H singlet), and multiplet for 10 H of the two benzene rings. ^{13}C NMR of the synthesized compound showed peaks at δ 41.62, 128.34, 128.58, 128.80, 134.99, 222.26 which match with the values in the literature. Elemental analysis of the synthesized compound confirmed the formation of the dibenzyl trithiocarbonates with good match between the experimental and the calculated values for the elements.

Further, the reaction was optimized with respect to the solvent, reaction time and the amount of the choline hydroxide. The model reaction was carried out in the presence of the solvents like water (H_2O), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), tetrahydro furan (THF), methyl alcohol (CH_3OH), Polyethylene glycol (PEG) and solvent free conditions at room temperature. The results obtained in terms of time and % yield are summarized in table 1.

Table 1. Time and % yield of model reaction with different solvent

S. No	Solvent	Time in min	% Yield
1	H_2O	15	94
2	DMSO	80	62
3	DMF	150	45
4	THF	160	20
5	CH_3OH	140	46
6	PEG	160	48
7	Absence of solvent	250	No reaction

Further the reaction was examined for the optimal amount of the phase transfer catalyst choline hydroxide. It was found that the yield of the reaction was directly dependent on the amount of the catalyst used. Maximum yield of the reaction was obtained for the 3.0 equivalent of choline hydroxide. Yield of the reaction was found to be 80 % and 65% at 2.5 and 2.0 equivalent of the choline hydroxide respectively.

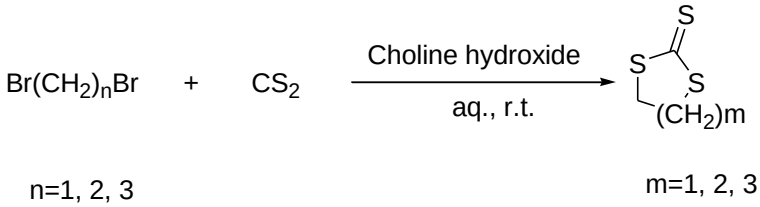
Model reaction was explored with the various other phase transfer catalyst in aqueous medium for the synthesis of the symmetrical trithiocarbonates. It was found that the maximum yield of the reaction was found in the choline hydroxide (Table 2)

Table 2. Time and % yield of model reaction with different phase transfer catalyst in aqueous medium

S. No	Phase transfer catalyst	Time in min	% Yield
1	Amberlyst A-26	180	38
2	Choline hydroxide	15	94
3	Tetrabutyl ammonium bromide (TBAB)	200	18
4	Tetrabutyl ammonium hydroxide (TBH)	120	46
5	Tetra-n-butyl ammonium hydrogen sulfate (TBAHS)	160	35
6	Potassium *O*-ethyl dithiocarbonate	240	15
7	Absence of catalyst	250	No reaction

After optimizing the reaction for the synthesis of the model dibenzyl trithiocarbonates a variety of the symmetrical trithiocarbonates were synthesized by reacting various alkyl aryl-alkyl and aryl halide with CS_2 in the presence of the choline hydroxide at room temperature (Table 3).

This synthetic process worked efficiently with primary, secondary, and allyl halides with excellent yield giving the trithiocarbonates as sole product. It was found that the reaction went good with the aryl halides and the tertiary alkyl halides, but the yield here was less and the reaction time was longer. The process was extended for the synthesis of the cyclic trithiocarbonates with the terminal dihalides and found to give good response without any by-product (Scheme 2).

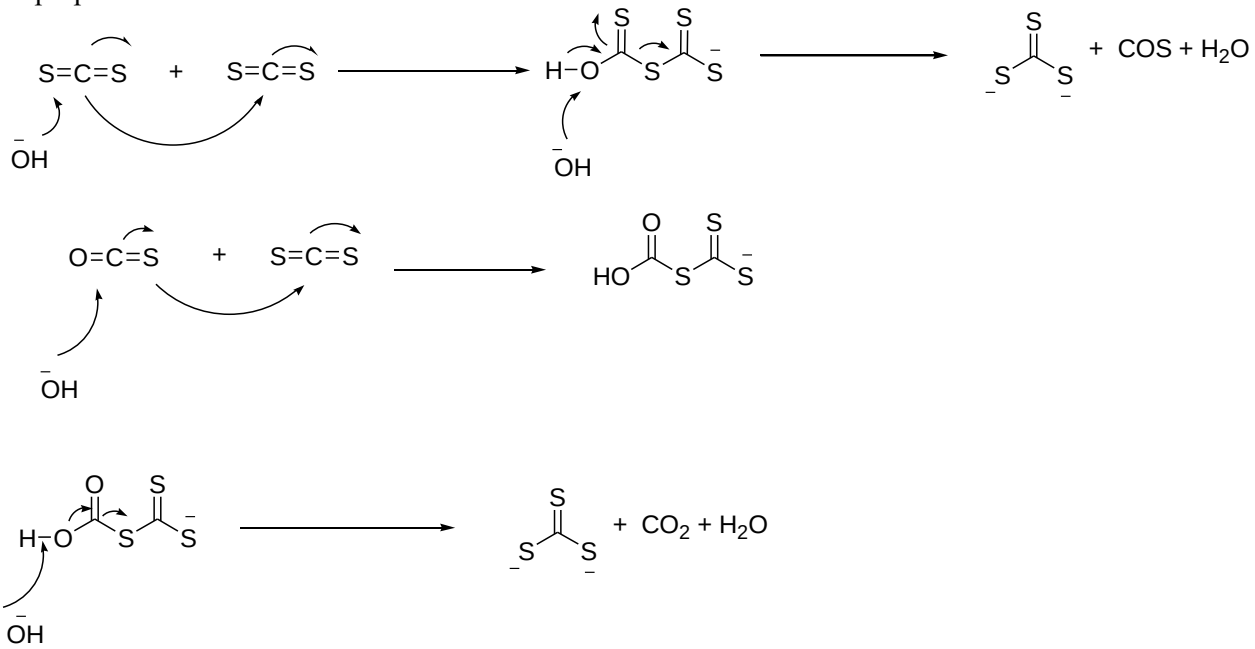


Scheme 2 Synthesis of cyclic trithiocarbonates

Table 3. Synthesis of various trithiocarbonates

Entry	Alkyl halide	Time	% Yield	Ref
a	Benzyl chloride	15	94	30
b	Allyl	20	92	28
c	Ethyl	25	90	28
d	*n*-butyl	20	96	27
e	*n*-propyl	20	92	27
f	1-Chloro ethyl benzene	25	91	29
g	*sec*-Butyl chloride	30	80	29
h	*tert*-Butyl chloride	50	40	29
i	*iso*-Propyl bromide	40	80	29
j	PhBr	50	30	29
k	$BrCH_2CH_2Br$	50	88	30
l	$BrCH_2CH_2CH_2Br$	60	84	33
m	$BrCH_2CH_2CH_2CH_2Br$	120	88	33

The proposed reaction mechanism is shown in scheme 3



Scheme 3 Proposed mechanism of the reaction

3. Experimental

3.1Reagents and Instruments

The synthesis work was done with the reagents purchased from Sigma Aldrich and Merck. The synthetic products formed were recognized by collating spectra and other data found in the literature. Bomem MB-FTIR machinewas used for the IR characterizing the synthesized compound while Bruker Advance spectrometer was employed for the NMR spectra (400 MHz& 100 MHz) in $CDCl_3$. Carlo-Erba EA 1110 analyzer was used for the elemental analysis of compounds. The

synthesized compounds were structurally identified with the help of IR, NMR and elemental analysis.

3.2General Procedure

A clean and dry RB flask was charged with 3.0 mmols of choline hydroxide and 2 mmols of CS_2 in aqueous medium and stirred for 5 minutes at room temperature until the appearance of the red color. Now 2.0 mmols of benzyl chloride was added and stirred for further 10 minutes. The progress of the reaction is ascertained with the thin layer chromatography (TLC). The pure compound dibenzyl trithiocarbonate was obtained by the column chromatography using *n*-hexane.

3.3Data for the synthesized compound

i. ***Dibenzyltrithiocarbonate***(1) Lemonycoloroil;^{1}H NMR (ppm) δ 4.70(4H singlet),7.29-7.39 (10H multiplet), IR (cm^{-1})1059 (S=C), ^{13}C NMR (ppm) δ 40.98, 127.84, 129.02, 129.20, 135.04, 221.98; Elemental analysis for $C_{15}H_{14}S_3$ element, found(calculated); C, 62.04 (61.99); H, 4.83 (4.79); S= 33.12 (32.99). MS (ESI)for $C_{15}H_{14}S_3$ m/e= 290.02, Calculated= 290.46.

ii. ***Diallyltrithiocarbonate*** (2) Mustard color oil; NMR ^{1}H; (ppm) δ 4.09 (4H, doublet), 5.18 (2H doublet), 5.29 (2H doublet), 5.80-5.90 (2H multiplet), IR (cm^{-1}) 1058 (S=C), ^{13}C NMR (ppm) δ 40.02, 120.06, 130.98, 22.48; Elemental analysis for $C_7H_{10}S_3$: element, found (calculated) %; C, 44.17 (44.19); H, 5.20 (5.18), S, 50.54 (50.49). Molecular mass MS (ESI)for$C_7H_{10}S_3$m/e=189.94, Calculated = 190.34.

iii. ***Diethyl trithiocarbonate***(3) Canary yellow oil; ^{1}H NMR (ppm) δ 1.50 (6H triplet), 3.50 (4H, quartet), IR (cm^{-1})1070 (S=C), ^{13}C NMR (ppm) δ 12.89, 31.03, 222.90; Elemental analysis for $C_5H_{10}S_3$: element, found (calculated)%; C, 36.10 (36.11); H, 5.98(6.02); S 57.98 (58.01). Molecular mass MS (ESI)for$C_5H_{10}S_3$ m/e= 165.99, Calculated=166.33.

iv. ***Dibutyltrithiocarbonate*** (4) Husk color oil; ^{1}H NMR (ppm) δ 1.01 (6H triplet), 1.50-1.50(4H multiplet), 3.39(4H triplet); IR (cm^{-1})1048 (S=C); ^{13}C NMR (ppm) δ 13.58 22.02, 29.98, 36.60, 225.01; Elemental analysis for $C_9H_{18}S_3$:element, found(calculated)%; C, 47.90 (48.16); H,8.18 (8.16); S, 43.30 (43.19). Molecular mass MS (ESI) for $C_9H_{18}S_3$m/e= 222.05, Calculated= 222.43.

v. ***Dipropyltrithiocarbonate*** (5) Yellow oil;^{1}H NMR (ppm) δ 1.508 (6H triplet), δ 3.50(4H quintet), IR (cm^{-1})1072 (S=C), ^{13}C NMR (ppm) δ 13.01, 31.02, 222.98; Elemental analysis for $C_7H_{14}S_3$: element, found (calculated) %; C, 42.94 (43.29); H, 8.72 (8.52); S, 49.07 (49.48). Molecular mass MS (ESI) for$C_7H_{14}S_3$m/e = 194.02, Calculated=194.38.

vi. ***Bis(1-phenyl ethyl) Trithiocarbonate*** (6) Light yellow oil;^{1}H NMR (ppm) δ 1.79 (6H doublet), 5.40(2H quintet), 7.18-7.28 (10H multiplet); IR (cm^{-1})1068, 1452, 1488, 1601 cm^{-1} (S=C), ^{13}C NMR (ppm) δ 20.99, 49.24, 128.12, 128.86, 144.01, 221.02; Elemental analysis for $C_{17}H_{18}S_3$: element, found (calculated)%; C 63.48 (63.98); H, 5.68 (5.70); S, 30.24 (30.20). Molecular mass MS (ESI) for $C_{17}H_{18}S_3$m/e= 318.05, Calculated=318.52.

vii. ***Sec-Butyltrithiocarbonate*** (7) Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.97(12H doublet), 2.11(2H multiplet), 2.83(4H doublet); IR (cm^{-1})1048 (S=C); ^{13}C NMR (ppm) δ 20.62, 29.00, 43.10, 208.63; Elemental analysis for $C_9H_{18}S_3$:element, found(calculated)%; C, 48.07 (47.98); H,8.18 (8.16); S, 43.30 (43.42). Molecular mass of $C_9H_{18}S_3$ = 222.43. m/e= 222.05

viii. ***Tert-Butyltrithiocarbonate***(8) Yellowish oil; ^{1}H NMR (ppm) δ 1.41(18 H Singlet); IR (cm^{-1})1052 (S=C); ^{13}C NMR (ppm) δ 30.20, 40.80; Elemental analysis for $C_9H_{18}S_3$: element, found(calculated) %; C, 48.32 (48.60); H,8.15 (8.16); S, 43.24 (43.24). Molecular mass MS (ESI) for $C_9H_{18}S_3$ m/e= 222.05, Calculated = 222.41.

ix. ***Di iso-propyltrithiocarbonate*** (9) Yellowish oil;1H NMR (ppm) δ 1.36 (12H doublet), 2.88(2H multiplet), IR (cm^{-1})1065 (C=S), ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 23.1, 36.2, 223.04; Elemental analysis for $C_7H_{14}S_3$: element, found (calculated)%; C, 43.02 (43.25); H, 7.19 (7.26); S,49.07 (49.50). Molecular mass MS (ESI) for$C_7H_{14}S_3$m/e=194.02, Calculated = 194.38.

x. ***Diphenyltrithiocarbonate*** (10) Pale yellowish oil; ^{1}H NMR (ppm) δ 7.28-7.51 (10H multiplet), IR (cm^{-1}) 1070 (S=C), ^{13}C NMR (ppm) δ 128.34, 128.58, 128.80, 134.99, 222.26; elemental analysis for $C_{13}H_{10}S_3$ element, found(calculated); C, 59.34 (59.06); H, 3.84 (3.82); S= 36.66 (36.10). Molecular mass MS (ESI) for$C_{13}H_{10}S_3$m/e= 261.99, Calculated = 262.41.

xi. ***1,3-Dithiolane-2-thione*** (11): yellow oil; ^{1}H NMR (ppm) δ 4.02 (4H, singlet); ^{13}C NMR (ppm) δ 228.2, 44.8; elemental analysis of $C_3H_4S_3$found (calculated)%: C, 26.31(26.18); H, 3.95(3.91); S, 70.60 (70.38). Molecular mass MS (ESI) for$C_3H_4S_3$ m/e=135.94, = Calculated 136.25.

xii. ***1,3-Dithiane-2-thione*** (12) Lemony oil; ^{1}H NMR (ppm) δ 3.18 (4H triplet, J = 1.6 Hz), 2.38 (2H multiplet). ^{13}C NMR (ppm) δ 218.0, 36.0, 20.5; elemental analysis of $C_4H_6S_3$found (calculated)%: C,31.97(31.53); H, 4.02(4.06); S, 64.01(63.25); Molecular mass MS (ESI) for $C_4H_6S_3$m/e= 149.96, Calculated =150.28

xiii. ***1,3-Dithiepane-2-thione*** (13), yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (m, 4H), 1.96(m, 4H); IR (cm^{-1}): 1058 (S=C); ^{13}C NMR (ppm) δ 29.8, 35.8, 210; elemental analysis of $C_5H_8S_3$ found (calculated)%: C, 36.54 (36.55); H 4.906(4.91); S, 58.20(58.54). Molecular mass MS (ESI) for $C_5H_8S_3$ m/e=163.97, Calculated = 164.31.

4. Conclusions

A novel, cleaner, greener, energy saving, and efficient method has been developed for the synthesis of biologically potent organosulfur compound in terms of trithiocarbonates. This method involves the use of choline hydroxide which is a water-soluble base which also acts as a phase transfer catalyst for the synthesis of the trithiocarbonates in the aqueous medium. The process is economical and a step toward sustainable development in the field of organic synthesis.

Conflict of Interest

The authors declare that there is no conflict of interest regarding this manuscript.

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