Triton-B Catalyzed, Green and Efficient Method for the Synthesis of Dithiocarbazates

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A novel, solvent free and high yielding method was accomplished for one-pot synthesis of dithiocarbazates by the reaction of various alkyl halides (primary, secondary and tertiary) with variety of substituted hydrazines using Triton-B (benzyl-trimethylammonium hydroxide) and carbon di sulphide. This new method of synthesizing dithiocarbazates involves mild conditions, simple procedures and high yields of the products as compared to previously used methods.

Keywords: Primary alkyl halides, Secondary alkyl halides, Tertiary alkyl halides, Triton-B, Carbon disulfide, Dithiocarbazates.

INTRODUCTION

Organic dithiocarbazates have invited research attention due to their impeccable chemistry and wild utility. They have pivotal role in pharmaceutical, industrial applications and as organic and inorganic synthon [1-5]. The thiocarbamoyl structure of dithiocarbazate shows various biological activities like antibacterial, antifungal, anti-inflammatory and uncoupling activity [6]. Their extensive use in pharmaceuticals [7-9], agrochemicals [10], organic synthesis [11-13], coordination chemistry [14-16] peptide synthesis [17], solid phase organic synthesis [18] and complexation reactions with transition metals [19,20] make them a unique hetero compound. The donor ligand complexation reaction of dithiocarbazate with transition metal is of considerable interest due to high biological activity [21,22]. The unique hetero compound has shown considerable biological activity in pharmaceutical and agricultural industry [23,24]. They also show various activities like antifungal, antiprotazoal, antibacterial and anticancer activity [25].

Keeping in view their high utility it is necessary to develop a low-cost and high yielding method, hence, it is necessary to change their synthesis from costly and toxic chemicals like thiophosgene [26,27] and its derivatives [28,29] to the less toxic, low-cost and safe reagents like CS₂. Even, there were shortcomings with CS₂ also like harsh reaction conditions such as

use of strong bases, higher reaction temperatures and longer reaction times [30]. Thus, we became interested to introduce the improved methodologies. Considering the high utility of dithiocarbazates, we report here an efficient, green and solvent-free synthesis of dithiocarbazates from the various alkyl halides (primary, secondary and tertiary) with variety of substituted hydrazines using Triton-B (benzyl-trimethylammonium hydroxide) and carbon disulphide.

EXPERIMENTAL

All the chemicals used were obtained from Merck, Aldrich and Fluka chemical companies. Reactions were carried out in nitrogen atmosphere. The structural analysis of compound was done as IR spectra (4000-200 cm⁻¹) on Bomem MB-104-FTIR spectrophotometer where as NMRs were scanned on AC-300F, NMR (300 MHz), instrument using CDCl₃ and some other deuterated solvents and TMS as internal standard. Elemental analysis was made by Carlo-Erba EA 1110-CNNO-S analyzer and the obtained values were in accordance with calculated values.

General procedure: To a solution of substituted hydrazine (3 mmol) and carbon disulfide (8 mmol) Triton-B (2 mmol) were slowly added while stirring at room temperature. The stirring was continued till 0.5 h after which required amount of alkyl halide (3 mmol) was added (**Scheme-I**). The reaction

Scheme-I

was further continued until the completion of reaction (Table-1) under argon. The obtained mixture was poured into water (20 mL) and the extraction of organic layer was done with EtOAc (3 × 10 mL). The organic layer was washed with 0.1 N hydrochloric acid (20 mL), sodium bicarbonate solution (25 mL), brine solution (30 mL) and dried sodium sulfate and concentrated to get the desired compound I. Later, the desired compounds were confirmed by IR, NMR and elemental analysis.

N'-Phenoxymethyl hydrazinecarbodithioic acid butyl ester (1): Yellow solid, m.p. 115 °C. ¹³C NMR (CDCl₃) δ = 13.2, 21.6, 32.2, 33.7, 43.5, 55.2, 112.2, 114.6, 134.2, 152.1, 222.3 (C=S) ppm; MS (EI): *m/z* = 270; IR (KBr, ν_{max}, cm⁻¹) = 674, 1211; ¹H NMR (400 MHz, CDCl₃) δ = 0.83 (t, 3H, *J* = 7.3 Hz), 1.31 (m, 2H), 1.82 (m, 2H), 2.1 (s, NH), 2.92 (t, 2H, *J* = 6.3 Hz), 3.70 (s, 3H), 4.02 (m, NH), 6.72-7.64 (m, 4H); Elemental analysis of C₁₂H₁₈N₂OS₂ calcd. (found) %: C, 53.29 (53.23); H, 6.70 (6.64); N, 10.36 (10.32); S, 23.72 (23.57).

N'-Phenethyl hydrazinecarbodithioic acid 3-phenylpropyl ester (2): Yellow solid, m.p. 120 °C. ¹³C NMR (CDCl₃) δ = 32.4, 33.2, 34.0, 112.1, 119.5, 125.4, 128.2, 129.1, 138.2, 221.1 (C=S) ppm; MS: *m/z* = 302; IR (KBr, ν_{max}, cm⁻¹) = 674, 1208; ¹H NMR (400 MHz, CDCl₃) δ = 2.01 (s, H, NH), 2.28 (m, 2H, Ph.CH₂.CH₂.CH₂-S), 2.50 (t, 2H, *J* = 7.2 Hz, Ph.CH₂), 2.82 (t, 2H, Ph.CH₂.CH₂.CH₂-S), 4.01 (m, H, Ph.NH), 6.64-7.10 (m, 10H, Ar-H); Elemental analysis of C₁₆H₁₈N₂S₂ calcd. (found) %: C, 63.53 (63.34); H, 6.00 (6.25); N, 9.25 (9.16); S, 21.21 (21.27).

N'-Butyl hydrazinecarbodithioic acid 3-phenylpropyl ester (3): Yellow solid, m.p. 124 °C. ¹³C NMR (CDCl₃) δ = 34.2, 37.1, 47.0, 49.5, 118.2, 192.3, 223.0 (C=S) ppm; MS: *m/z* = 288; IR (KBr, ν_{max}, cm⁻¹) = 673, 1203; ¹H NMR (400

MHz, CDCl₃) δ = 2.08 (s, H, NH), 3.17 (2H, t, *J* = 6.5 Hz, Ph.CH₂CH₂S), 3.21 (m, 2H, *J* = 7.2 Hz, PhCH₂), 4.50 (m, H, PhNH), 6.66-7.12 (m, 10H, Ar-H); Elemental analysis of C₁₅H₁₆N₂S₂ calcd. (found) %: C, 62.45 (62.71); H, 5.58 (6.63); N, 9.70 (9.58); S, 22.22 (22.11).

N'-Phenethyl hydrazinecarbodithioic acid 3-phenylpropyl ester (4): Yellow solid, m.p. 115 °C. ¹³C NMR (CDCl₃) δ = 13.4, 20.0, 31.2, 38.1, 50.6, 126.4, 127.2, 128.7, 141.6, 223.1 (C=S) ppm; MS: *m/z* = 254; IR (KBr, ν_{max}, cm⁻¹) = 675, 1208; ¹H NMR (400 MHz, CDCl₃) δ = 1.02 (t, 3H, CH₃), 1.31 (m, 2H, CH₂CH₃), 1.52 (m, 2H, CH₂.CH₂CH₃), 2.01 (br, NH), 2.62 (m, 2H, NHCH₂), 4.10 (s, 2H, PhCH₂), 7.02-7.12 (m, 5H, Ar-H); Elemental analysis of C₁₂H₁₈N₂S₂ calcd. (found) %: 56.64 (56.45); H, 7.12 (7.34); N, 11.00 (11.26); S, 25.20 (25.11).

N'-Butyl hydrazinecarbodithioic acid 1-methyl butyl ester (5): Yellow solid, m.p. 122 °C. ¹³C NMR (CDCl₃) δ = 10.4, 13.5, 20.5, 21.1, 31.3, 32.5, 40.3, 49.7, 223.2 (C=S) ppm; MS: *m/z* = 220; IR (KBr, ν_{max}, cm⁻¹) = 681, 1212; ¹H NMR (400 MHz, CDCl₃) δ = 0.97 (t, 3H, CH₃), 1.03 (t, 3H, CH₃), 1.31 (m, 2H, CH₂.CH₃), 1.39 (d, 3H, CHCH₃), 1.51 (m, 2H, CH₃CH₂CH₂), 1.93 (m, 2H, CHCH₂), 2.02 (br, H, NH), 2.61 (m, 2H, NHCH₂), 2.73 (m, H, CH-S); Elemental analysis of C₉H₂₀N₂S₂ calcd. (found) %: 49.04 (49.32); H, 9.14 (9.00); N, 12.70 (12.74); S, 29.11 (29.31).

N'-(3-Nitrophenyl)hydrazinecarbodithioic acid 4-methoxybenzyl ester (6): Yellow solid, m.p. 118 °C. ¹³C NMR (CDCl₃) δ = 38.1, 56.5, 107.3, 114.2, 118.2, 128.7, 129.7, 133.9, 143.9, 148.8, 160.8, 223.5 (C=S) ppm; MS: *m/z* = 349; IR (KBr, ν_{max}, cm⁻¹) = 679, 1215; ¹H NMR (400 MHz, CDCl₃) δ = 2.01 (br, H, NHPh.OMe), 3.76 (s, 3H, OCH₃), 4.09 (br, H, NHPh.NO₂), 6.67-7.63 (m, 8H, Ar-H); Elemental analysis of

TABLE-1
CONVERSION OF ALKYL HALIDES INTO PROTOTYPE OF GENERAL FORMULA I

Compd.	R ₁	R ₂	R ₃	X	R	Time (h)	Yield (%)
1	<i>n</i> -C ₃ H ₇	H	H	Br	4-MeO-Ph	2.0	93
2	Phenyl ethyl	H	H	Br	Phenyl	2.0	96
3	Phenyl methyl	H	H	Cl	Phenyl	2.5	86
4	Phenyl	H	H	Cl	Butyl	3.0	91
5	C ₂ H ₅	Me	H	Br	Butyl	3.0	89
6	4-MeO.Ph	H	H	Cl	3-NO ₂ .Ph	3.0	84
7	C ₃ H ₇	H	H	Br	4-NO ₂ .Ph	3.0	85
8	C ₃ H ₇	H	H	Br	2,4-NO ₂ .Ph	3.0	82
9	C ₃ H ₇	H	H	Br	Naphthyl	3.0	82
10	C ₄ H ₉	C ₄ H ₉	H	Br	Phenyl	3.0	88
11	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	Br	Phenyl	3.0	86
12	C ₃ H ₁₁	H	H	Cl	Butyl	2.5	95
13	C ₃ H ₁₅	H	H	Cl	Phenyl	2.5	95
14	C ₆ H ₁₉	H	H	Cl	Butyl	2.0	98
15	C ₃ H ₇	C ₃ H ₇	H	Br	Phenyl	3.0	85
16	Phenyl	CH ₃	H	Br	Phenyl	3.0	82

$C_{15}H_{15}N_3O_3S_2$ calcd. (found) %: C, 51.55 (51.22); H, 4.32 (4.51); N, 12.02 (12.23); S, 18.34 (18.02).

***N'*-(4-Nitrophenyl) hydrazinecarbodithioic acid butyl ester (7):** Yellow solid, m.p. 121 °C. ^{13}C NMR ($CDCl_3$) δ = 13.5, 21.2, 32.4, 33.5, 113.9, 124.3, 138.7, 143.1, 223.3 (C=S) ppm; MS: m/z = 285; IR (KBr, ν_{max} , cm^{-1}) = 668, 1201; 1H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, 3H, CH_3), 1.31 (m, 2H, CH_2CH_3), 1.92 (m, 2H, SCH_2CH_2), 2.09 (br, H, NH), 2.82 (t, 2H, SCH_2), 4.01 (br, N, $NHArNO_2$), 6.95-8.15 (m, 4H, Ar-H); Elemental analysis of $C_{11}H_{15}N_3O_3S_2$ calcd. (found) %: C, 46.28 (46.44); H, 5.31 (5.16); N, 14.71 (14.46); S, 22.46 (22.20).

***N'*-(2,4-Nitrophenyl) hydrazinecarbodithioic acid butyl ester (8):** Yellow solid, m.p. 108 °C. ^{13}C NMR ($CDCl_3$) δ = 13.5, 21.7, 32.1, 33.9, 113.9, 119.1, 130.4, 132.6, 139.9, 143.1, 222.7 (C=S) ppm; MS: m/z = 330; IR (KBr, ν_{max} , cm^{-1}) = 671, 1214; 1H NMR (400 MHz, $CDCl_3$) δ = 0.96 (t, 3H, CH_3), 1.34 (m, 2H, CH_2CH_3), 1.97 (m, 2H, SCH_2CH_2), 2.06 (br, H, NH), 2.86 (t, 2H, SCH_2), 4.08 (br, N, $NHArNO_2$), 7.16-9.52 (m, 3H, Ar-H); Elemental analysis of $C_{11}H_{14}N_4O_4S_2$ calcd. (found) %: C, 39.98 (40.21); H, 4.26 (4.04); N, 16.95 (16.75); S, 19.40 (19.51).

***N'*-(1,4,4a,8a-Tetrahydronaphthalen-1-yl) hydrazine carbodithioic acid butyl ester (9):** Yellow solid, m.p. 120 °C. ^{13}C NMR ($CDCl_3$) δ = 13.7, 22.5, 32.7, 33.7, 107.2, 117.4, 121.6, 124.7, 126.8, 127.6, 133.8, 142.8, 224.4 (C=S) ppm; MS: m/z = 290; IR (KBr, ν_{max} , cm^{-1}) = 678, 1207; 1H NMR (400 MHz, $CDCl_3$) δ = 0.93 (t, 3H, CH_3), 1.31 (m, 2H, CH_2CH_3), 1.95 (m, 2H, SCH_2CH_2), 2.04 (br, H, NH), 2.81 (t, 2H, SCH_2), 4.07 (br, N, $NHArNO_2$), 6.77-7.53 (m, 7H, Ar-H); Elemental analysis of $C_{15}H_{18}N_2S_2$ calcd. (found) %: C, 62.02 (62.43); H, 6.24 (6.32); N, 9.63 (9.52); S, 22.07 (22.24).

***N'*-Phenyl hydrazinecarbodithioic acid 1-butylpentyl ester (10):** Yellow solid, m.p. 123 °C. ^{13}C NMR ($CDCl_3$) δ = 14.4, 23.3, 28.7, 36.4, 41.6, 112.4, 119.5, 129.2, 142.6, 223.6 (C=S) ppm; MS: m/z = 310; IR (KBr, ν_{max} , cm^{-1}) = 675, 1210; 1H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, 6H, CH_3), 1.27 (m, 4H, CH_2CH_2CH), 1.36 (m, 4H, CH_2CH_3), 1.94 (m, 4H, $CHCH_2$), 2.07 (br, H, NH), 2.54 (t, H, SCH), 4.07 (br, H, $NHAr$), 6.64-7.16 (m, 5H, Ar-H); Elemental analysis of $C_{16}H_{26}N_2S_2$ calcd. (found) %: C, 61.88 (61.76); H, 8.43 (8.53); N, 9.01 (9.21); S, 20.64 (20.45).

***N'*-Phenyl hydrazinecarbodithioic acid 1,1-dibutylpentyl ester (11):** Yellow solid, m.p. 116 °C. ^{13}C NMR ($CDCl_3$) δ = 14.2, 23.6, 26.9, 39.4, 41.3, 112.7, 119.5, 129.9, 142.4, 223.7 ppm; MS: m/z = 366; IR (KBr, ν_{max} , cm^{-1}) = 667, 1214; 1H NMR (400 MHz, $CDCl_3$) δ = 0.92 (t, 6H, CH_3), 1.27 (m, 4H, CH_2CH_2C), 1.31 (m, 4H, CH_2CH_3), 1.87 (m, 4H, $CHCH_2$), 2.02 (br, H, NH), 4.2 (br, H, $NHAr$), 6.65-7.17 (m, 5H, Ar-H); Elemental analysis of $C_{20}H_{34}N_2S_2$ calcd. (found) %: C, 65.51 (65.26); H, 9.34 (9.10); N, 7.63 (7.43); S, 17.48 (17.48).

***N'*-Butyl-hydrazinecarbodithioic acid hexyl ester (12):** Yellow solid, m.p. 118 °C. ^{13}C NMR ($CDCl_3$) δ = 13.5, 14.2, 20.4, 23.3, 28.3, 31.7, 32.9, 49.7, 223.3 ppm; MS: m/z = 248; IR (KBr, ν_{max} , cm^{-1}) = 676, 1206; 1H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, 6H, CH_3), 1.27 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.36 (t, 2H, CH_2CH_3), 1.51 (m, 2H, $NHCH_2CH_2$), 1.92 (m, 2H, SCH_2CH_2), 2.1 (br, 2H, NH), 2.63 (t, 2H, $NHCH_2$), 2.85 (t, 2H, SCH_2); Elemental analysis of $C_{11}H_{24}N_2S_2$ calcd. (found) %: C, 53.17 (53.32); H, 9.73 (9.53); N, 11.27 (11.38); S, 25.80 (25.63).

***N'*-Phenyl hydrazinecarbodithioic acid octyl ester (13):** Yellow solid, m.p. 120 °C. ^{13}C NMR ($CDCl_3$) δ = 14.3, 23.12, 28.7, 30.3, 31.3, 32.7, 112.4, 129.8, 118.7, 142.4, 223.8 ppm; MS: m/z = 296; IR (KBr, ν_{max} , cm^{-1}) = 677, 1213; 1H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, 3H, CH_3), 1.27 (m, 8H, CH_2), 1.31 (m, 2H, CH_2CH_3), 1.98 (m, 2H, SCH_2CH_2), 2.04 (br, H, NH), 2.86 (t, 2H, SCH_2), 4.04 (br, H, Ph.NH), 6.63-7.24 (m, 5H, Ar-H); Elemental analysis of $C_{15}H_{24}N_2S_2$ calcd. (found) %: C, 60.75 (60.54); H, 8.15 (8.32); N, 9.44 (9.31); S, 21.62 (21.76).

***N'*-Butyl hydrazinecarbodithioic acid decyl ester (14):** Yellow solid, m.p. 120 °C. ^{13}C NMR ($CDCl_3$) δ = 13.5, 14.7, 20.6, 23.3, 28.7, 30.8, 30.7, 31.7, 32.3, 222.3 ppm; MS: m/z = 304; IR (KBr, ν_{max} , cm^{-1}) = 676, 1224; 1H NMR (400 MHz, $CDCl_3$) δ = 0.95 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.27 (m, 12H, CH_2), 1.32 (m, 4H, CH_2CH_3), 1.51 (m, 2H, $CH_2CH_2CH_3$), 1.92 (m, 2H, SCH_2CH_2), 2.03 (br, 2H, NH.NH), 2.61 (m, 2H, $NHCH_2$), 2.85 (t, 2H, SCH_2); Elemental analysis of $C_{15}H_{32}N_2S_2$ calcd. (found) %: C, 59.14 (59.31); H, 10.58 (10.33); N, 9.21 (9.20); S, 21.05 (21.23).

***N'*-Phenyl hydrazinecarbodithioic acid 1-propylbutyl ester (15):** Yellow solid, m.p. 123 °C. ^{13}C NMR ($CDCl_3$) δ = 14.3, 20.11, 38.6, 40.6, 112.7, 118.6, 129.8, 143.6, 222.3 ppm; MS: m/z = 282; IR (KBr, ν_{max} , cm^{-1}) = 674, 1212; 1H NMR (400 MHz, $CDCl_3$) δ = 0.96 (s, 3H, CH_3), 1.31 (m, 4H, CH_2CH_3), 1.90 (m, 4H, $CHCH_2$), 2.01 (br, H, NH), 2.50 (m, H, $CH-S$), 4.13 (br, H, NH-Ar), 6.64-7.21 (m, 5H, Ar-H); Elemental analysis of $C_{14}H_{22}N_2S_2$ calcd. (found) %: C, 59.52 (59.74); H, 7.84 (7.65); N, 9.91 (9.91); S, 22.71 (22.43).

***N'*-Phenyl hydrazinecarbodithioic acid 1-phenylethyl ester (16):** Yellow solid, m.p. 121 °C. ^{13}C NMR ($CDCl_3$) δ = 23.6, 41.3, 112.7, 118.7, 126.7, 128.7, 129.5, 141.6, 142.4, 222.3 ppm; MS: m/z = 288; IR (KBr, ν_{max} , cm^{-1}) = 677, 1212; 1H NMR (400 MHz, $CDCl_3$) δ = 1.67 (d, 3H, CH_3), 2.4 (br, H, NH), 3.97 (m, H, $CH-S$), 4.4 (br, H, NH-Ar), 6.64-7.26 (m, 10H, Ar-H); Elemental analysis of $C_{15}H_{16}N_2S_2$ calcd. (found) %: C, 62.45 (62.32); H, 5.58 (5.45); N, 9.70 (9.98); S, 22.22 (22.35).

RESULTS AND DISCUSSION

We are continuously working on the use of Triton-B for the improved synthesis of sulphur compounds like carbamates, dithiocarbamates and dithiocarbonates (xanthates). Here we are reporting novel, solvent free and high yielding method was accomplished for one-pot synthesis of dithiocarbazates by the reaction of various alkyl halides (primary, secondary and tertiary) with variety of substituted hydrazines using Triton-B (benzyl-trimethylammonium hydroxide) and carbon disulphide. Thus, Triton-B was added to the mixture of substituted hydrazine and carbon disulphide. After stirring the reaction for 30 min at room temperature, corresponding alkyl halide was added in it. The reaction was allowed to proceed and progress was checked by TLC (Table-1).

The synthesized compound was finally confirmed by IR and NMR spectral analysis. The ^{13}C NMR spectra of the synthesized compounds seems to show a peak between 222 ppm to 224 ppm for dithio-bonding (C=S) found in dithiocarbazate. The presence of $-CH_3$ group is thought to be shown by singlet at δ = 0.96 and $-CH_2CH_3$ by multiplet at δ = 1.32 in the final product. Compounds **2**, **3**, **4**, **6**, **7**, **13**, **15** and **16** show a sharp

peak at ($\delta = 4$ to 4.01) due to presence of aromatic ring in alkyl halides. In compounds **1** and **2** the presence of multiplet at $\delta = 4$ seems to be due to presence of -NH group.

According to proposed reaction mechanism S^- of the dithiocarbazate ion produced attacks to the electrophilic carbon of the corresponding alkyl halide to produce dithiocarbazates in appreciable yields (82-98 %) at room temperature in 2-3 h (Table-1). The progress of reaction was successful and the isolated products were further confirmed by various spectroscopic and analytical techniques. The extraction procedures of products were simple and obtained by concentration of organic layer after filtration of basic resin from the reaction.

In order to get better results several solvents like *n*-heptane, *n*-hexane, acetonitrile, benzene, toluene, methanol, dichloromethane, chloroform, DMSO, dimethylformamide and hexamethylphosphoric triamide were tried. Previously, the synthesis of dithiocarbazates through the same mechanism has also been reported but the procedure was not solvent free. In order to enhance the efficiency of synthesis of dithiocarbamates we tried the same reaction in the absence of solvent and found that desired product can be isolated in higher yields.

Conclusion

In conclusion, we have accomplished a novel, solvent free and high yielding method for one-pot synthesis of dithiocarbazates by the reaction of various alkyl halides (primary, secondary and tertiary) with variety of substituted hydrazines using Triton-B (benzyl-trimethylammonium hydroxide) and carbon disulphide. The high yields of corresponding dithiocarbazates makes it a better method. Furthermore, this method exhibits greener methodology, mild reaction conditions and experimental convenience.

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CONFLICT OF INTEREST

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

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