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RESEARCH ARTICLE

An efficient, basic resin mediated, one-pot synthesis of O-alkyl-S-methyl dithiocarbonates from the corresponding alcohols

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A novel process for the one-step conversion of primary and secondary alcohols into their O-alkyl-S-methyl dithiocarbonates was developed using Amberlite IRA 400 (basic resin) in presence of carbon disulfide. O-Alkyl-S-methyl dithiocarbonates of various alcohols were isolated in very good to excellent yields. This protocol is mild and efficient compared to other existing methods.

Keywords: Amberlite IRA 400; Carbon disulfide; Alcohols; Dithiocarbonates; Thiocarbamation

1. Introduction

O-Alkyl-S-methyl dithiocarbonates (xanthates) have been frequently used as a versatile source of radicals [1–4], versatile intermediates in the synthesis of thiols [5], thiocarbonates [6, 7], alkenes [8, 9], alkanes [10], S-activated carbanion [11, 12] and photosensitizers [13] for the polymerization of vinyl monomers. They have also been used in the synthesis of natural products [14], Claisen rearrangement [15–17] and played important roles due to their biological activities [18]. Traditionally, they are prepared from alcohol in a three-step process [19]. The reaction involves the use of strong bases such as sodium hydride, sodium amide or potassium *t*-butoxide in polar aprotic solvents like DMSO [20], DMF [21], or *diglyme* [22]. Phase transfer catalysis and crown ethers have also been used with strong bases specifically for the preparation of dithiocarbonates from unfunctionalized alcohols [23]. However, most of these methods suffer from limitations such as longer reaction times, use of expensive strongly basic reagents and tedious work-up. Consequently, there is continued interest in developing new and convenient methods for the synthesis of dithiocarbonates using mild reaction conditions. Our group has been engaged for several years in the development of new methodologies for the preparation of carbamates and dithiocarbamates using cheap, abundantly available

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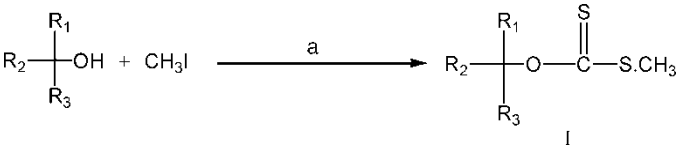
and safe reagents [24–28]. Recently [29, 30], we found that Amberlite IRA 400 (basic resin) is the best reagent for the preparation of carbamates and dithiocarbamates using cheap, abundantly available and safe reagents like CO_2 and CS_2, respectively. Furthermore, use of basic resin has also been reported [31] for the tetrahydropyranylation of alcohols and phenols. In the present communication, we report herein an efficient, one-pot, novel synthesis of O-alkyl-S-methyl dithiocarbonates from corresponding alcohols and methyl iodide using basic resin/CS_2 system.

2. Results and discussion

During the course of our recent studies for the synthesis of carbamates and dithiocarbamates Amberlite IRA 400 (basic resin) was found to be an efficient and mild basic catalyst [29, 30]. Taking these observations as a guide, we tried a reaction of an alcohol with methyl iodide using basic resin/CS_2 system at room temperature. The reaction proved to be successful and the desired products were isolated and further confirmed by various spectroscopic and analytical techniques. Thus, various alcohols were reacted with methyl iodide using basic resin/CS_2 system at room temperature for 2–6 h afforded O-alkyl, S-methyl dithiocarbonates in high yields (72–98%) as shown in table 1. The whole reaction plan is shown in scheme 1.



I

SCHEME 1 Reagents and conditions: (a) Amberlite IRA 400, CS_2, Dry DMSO, rt, 2–6 h.

Table 1. Conversion of alcohols into O-alkyl, S-methyl dithiocarbonates **I**.

Entry	R_1	R_2	R_3	Time (h)	Isolated yield (%)	Reference
1	CH_3	H	H	2.5	90	[32]
2	$CH_3(CH_2)_6$	H	H	2	93	[33]
3	$CH_3(CH_2)_{10}$	H	H	2	95	[34]
4	$CH_3(CH_2)_{14}$	H	H	2	98	[35]
5	$(CH_3)_2{\cdot}CH{\cdot}CH_2$	H	H	2.5	92	[36]
6	CH_3	CH_3	H	2.5	85	[37]
7	Ph	H	H	2.5	91	[38]
8	$R_1 = R_2 = R_3 = Ph$			3	88	[39]
9	$R_1 = R_2 =$ Cyclohexyl		H	3	82	[40]
10	$Ph{\cdot}CH = CH$	H	H	2.5	80	
11	$Ph{\cdot}CH_2CH_2$	H	H	2.5	94	
12	$Ph{\cdot}CH_2$	CH_3	H	3	81	
13	n-C_3H_7	H	H	2	90	
14	$R_1 = R_2 =$ Menthyl		H	4	79	
15	$R_1 = R_2 =$ Cholesteryl		H	6	72	
16	n-C_4H_9	n-C_4H_9	H	3	78	
17	n-C_4H_9	n-C_4H_9	n-C_4H_9		not formed	

Note: All the products were characterized by IR, NMR and Mass spectroscopic data.

We tried several solvents including *n*-pentane, *n*-hexane, *n*-heptane chloroform, dichloromethane, benzene, methanol, DMF, DMSO, acetonitrile, HMPA etc. and found dry DMSO most suitable for the good yields of the required products at room temperature.

In conclusion, we have developed a convenient and efficient protocol for a one-pot, three components coupling of the various alcohols with methyl iodide in the presence of basic resin/CS_2 system. This reaction generates the corresponding O-alkyl, S-methyl dithiocarbonates in good to excellent yields. Further, this method exhibits substrate versatility, mild reaction conditions and experimental convenience. This synthetic protocol developed in our laboratory, is believed to offer a more general method for the formation of C-S bonds, essential to numerous organic syntheses.

3. Experimental

Chemicals were procured from Merck, Aldrich and Fluka chemical companies. Amberlite IRA 400 (basic resin) was also obtained from Merck. IR spectra (4000–200 cm^{-1}) were recorded on a Bomem MB-104 FTIR spectrophotometer where as ^1H NMRs were scanned on a AC-300F NMR (300 MHz) instrument using $CDCl_3$ as solvent and TMS as internal standard. Elemental analyses were made by Carlo-Erba EA1110 CNNO-S analyzer and agreed favorably with calculated values.

3.1 *Typical experimental procedure*

A mixture of 6 mmol alcohol and 6 mmol CS_2 were taken in 40 cm^3 dry *DMSO* and were allowed to stir for 20 minutes at room temperature. Basic resin (6 mmol) was added and the reaction was continued at r.t. for 1 h. Then 6 mmol of the methyl iodide was added. The reaction was further continued until completion (cf. table 1). The reaction mixture was filtered and filtrate was poured into 50 cm^3 distilled H_2O and extracted with ethyl acetate three times. The organic layer was separated, dried (Na_2SO_4), and concentrated to get the desired compound.

3.2 *O-Ethyl, S-methyl dithiocarbonate (1)*

Oil, IR (Neat) $\nu = 3000$–2900, 1230, $1065\ cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 1.40$–1.43 (t, 3H, J = 8.1 Hz, OCH_2CH_3), 2.54 (s, 3H, SCH_3), 4.54–4.57 (q, 2H, J = 8.2 Hz, OCH_2CH_3) ppm; MS: m/z = 136.

3.3 *O-Octyl, S-methyl dithiocarbonate (2)*

Oil, IR (Neat) $\nu = 3000$–2860, 1231, $1080\ cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 0.96$–1.56 (m, 15H of n-octyl group), 2.52 (s, 3H, SCH_3), 4.55–4.59 (t, 2H, J = 6.2 Hz, OCH_2 of n-octyl group) ppm; MS: m/z = 220.

3.4 *O-Dodecyl, S-methyl dithiocarbonate (3)*

Oil, IR (Neat) $\nu = 3000$–2850, 1240, $1082\ cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 0.94$–1.57 (m, 23H, CH_2 and CH_3 of n-dodecyl group), 2.54 (s, 3H, SCH_3), 4.60–4.63 (t, 2H, J = 7.2 Hz, OCH_2 of n-dodecyl group) ppm; MS: m/z = 276.

3.5 *O-Hexadecyl, S-methyl dithiocarbonate (4)*

Mp = 28.5 °C (ethanol); IR (KBr) ν = 3000–2855, 1238, 1081 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.95–1.67 (m, 31H, CH_3 and CH_2 of 31H of hexadecyl group), 2.53 (s, 3H, S*C*H_3), 4.61–4.64 (t, 2H, J = 6.2 Hz, O*C*H_2 of hexadecyl group) ppm; MS: m/z = 332.

3.6 *O-(3-Methylbutyl), S-methyl dithiocarbonate (5)*

Oil; IR (Neat) ν = 3000–2850, 1236, 1079 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.96 (d, 6H, J = 6.4 Hz, CH_3 of 3-methylbutyl group), 1.70–1.73 (m, 1H, CH of 3-methylbutyl group), 2.53 (s, 3H, S*C*H_3), 4.60–4.63 (t, 2H, J = 7.1 Hz, O*C*H_2 of 3-methylbutyl group) ppm; MS: m/z = 178.

3.7 *O-(1-Methylethyl), S-methyl dithiocarbonate (6)*

Oil; IR (Neat) ν = 3000–2900, 1238, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.36(d, 6H, J = 7.2 Hz, CH_3 of 1-methylethyl group), 2.53 (s, 3H, S*C*H_3), 5.76–5.79 (m, 1H, of 1-methylethyl group) ppm; MS: m/z = 150.

3.8 *O-Benzyl, S-methyl dithiocarbonate (7)*

Oil; IR (Neat) ν = 3100–2900, 1245, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.56 (s, 3H, S*C*H_3), 5.62 (s, 2H, Ph*C*H_2), 7.30–7.38 (m, 5H, Ar-H) ppm; MS: m/z = 198.

3.9 *O-Phenyl, S-methyl dithiocarbonate (8)*

Oil; IR (Neat) ν = 3100, 2950, 1600, 1500, 1200, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.57 (s, 3H, S*C*H_3), 7.20–7.25 (m, 5H, Ar-H) ppm; MS: m/z = 198.

3.10 *O-Cyclohexyl, S-methyl dithiocarbonate (9)*

Oil; IR (Neat) ν = 3000–2850, 1230, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.44–1.59 (m, 10H, CH_2 of cyclohexyl group), 2.54 (s, 3H, S*C*H_3), 5.60 (m, 1H, OC*H* of cyclohexyl group) ppm; MS: m/z = 190.

3.11 *O-Styryl, S-methyl dithiocarbonate (10)*

Oil; IR (Neat) ν = 3100, 2940, 1228, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.55 (s, 3H, S*C*H_3), 4.52 (d, 2H, J = 6.2 Hz, OCH_2), 6.60 (s, 1H, of C*H* = CH), 6.25 (s, 1H, of CH = C*H*), 7.15–7.30 (m, 5H, of Ar-H) ppm; ^{13}C NMR δ = 16.44, 70.33, 126.25, 127.73, 128.40, 135.20, 172.46 ppm. MS: m/z = 224, Analysis: $C_{11}H_{12}OS_2$, Calcd: C, 58.89; H, 5.39; S, 28.59; Obsd: C, 58.54; H, 5.58; S, 28.75.

3.12 *O-(3-Phenylpropyl), S-methyl dithiocarbonate (11)*

Oil; IR (Neat) ν = 3100–2955, 1232, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.80–1.82 (q, 2H, J = 7.2 Hz, $PhCH_2CH_2CH_2$), 2.52 (s, 3H, SCH_3), 2.60–2.63 (m, 2H, $PhCH_2$), 4.55–4.59 (t, 2H, J = 6.4 Hz, OCH_2 of 3-phenylpropyl group), 7.08–7.25 (m, 5H, Ar-H) ppm; ^{13}C NMR

δ = 16.40, 70.33, 31.88, 32.22, 67.34, 125.80, 128.30, 128.60, 138.80, 172.50 ppm. MS: m/z = 226. Analysis: $C_{11}H_{14}OS_2$, Calcd, C, 58.37; H, 6.23; S, 28.33; Obsd: C, 58.64; H, 6.35; S, 27.95.

3.13 *O-(1-methyl 2-Phenylethyl), S-methyl dithiocarbonate (12)*

Oil; IR (Neat) ν = 3100–2950, 1234, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.26 (d, 3H, J = 7.1 Hz, CH_3 of 1-methyl-2-phenethyl group), 2.54 (s, 3H, S*CH*$_3$), 2.76 (m, 2H, Ph*CH*$_2$), 3.82–3.85 (m, 1H, O*CH* of 1-methyl-2-phenethyl group), 7.10–7.20 (m, 5H, Ar-H), ppm; ^{13}C NMR δ = 16.43, 19.22, 42.30, 71.55, 125.80, 128.30, 128.60, 138.80, 172.50 ppm. MS: m/z = 226. Analysis: $C_{11}H_{14}OS_2$, Calcd, C, 58.37; H, 6.23; S, 28.33; Obsd: C, 58.55; H, 5.94; S, 28.59.

3.14 *O-n-Butyl, S-methyl dithiocarbonate (13)*

Oil, IR (Neat) ν = 3000–2900, 1235, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.93–0.96 (t, 3H, J = 7.5 Hz, CH_3 of n-butyl group), 1.33–1.48 (m, 4H, CH_2 of n-butyl group), 2.54 (s, 3H, S*CH3*), 4.20–4.25 (t, 2H, J = 8.2 Hz, O*CH*$_2$) ppm; ^{13}C NMR δ = 14.44, 15.89, 19.25, 32.56, 67.40, 172.22 ppm. MS: m/z = 164. Analysis: $C_6H_{12}OS_2$, Calcd, C, 43.86; H, 7.36; S, 39.04; Obsd: C, 43.44; H, 7.53; S, 39.34.

3.15 *O-Menthyl, S-methyl dithiocarbonate (14)*

Oil, IR (Neat) ν = 3000–2950, 1233, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85–0.87 (d, 3H, J = 7.2 Hz, CH_3 group of menthyl group), 0.90–0.95 (d, 6H, J = 8.0 Hz, $2CH_3$ of menthyl group), 1.15–2.20 (m, 8H, of menthyl group), 2.50 (s, 3H, SCH_3), 5.45–5.50 (m, 1H, OCH of menthyl group) ppm; ^{13}C NMR δ = 15.44, 20.11, 20.34, 20.47, 22.90, 24.40, 32.57, 66.80, 172.22 ppm. MS: m/z = 246 Analysis: $C_{12}H_{22}OS_2$, Calcd, C, 58.49; H, 9.00; S, 26.02; Obsd: C, 58.86; H, 8.83; S, 26.23.

3.16 *O-Cholesteryl, S-methyl dithiocarbonate (15)*

Mp = 125 °C, IR (KBr) ν = 3000–2850, 1241, 1082 cm^{-1}; ^1H NMR (DMSO) δ = 0.86–0.89 (d, 6H, J = 7.2 Hz, $2CH_3$ of isopropyl group of cholesteryl moiety), 0.90–0.95 (d, 3H, 6.4 Hz, CH_3), 1.10 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.21–2.20 (m, 31H, CH_2 of cholesteryl group), 2.54 (s, 3H, S*CH*$_3$), 3.50–3.53(m, 1H, O*CH* of cholesteryl group), 5.50–5.55 (m, 1H, C*H* = C in Cholesteryl group) ppm; ^{13}C NMR δ = 15.40, 18.50, 20.90, 22.33, 20.90, 21.64, 25.38, 28.50, 29.65, 30.20, 31.80, 32.20, 32.40, 39.40, 39.55, 35.96, 39.70, 40.55, 42.80, 46.44, 73.23, 122.84, 149.55, 172.28 ppm. MS: m/z = 476; Analysis: $C_{29}H_{48}OS_2$, Calcd, C, 73.05; H, 10.15; S, 13.45; Obsd: C, 72.75; H, 9.92; S, 13.86.

3.17 *O-sec-Butyl, S-methyl dithiocarbonate (16)*

Oil, IR (Neat) ν = 3000–2950, 1237, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.93–0.96 (t, 6H, $2CH_3$ of n-butyl), 1.29–1.33 (m, 8H, CH_2 of n-butyl), 1.44–1.49 (m, 4H, CH_2 of n-butyl), 2.55 (s, 3H, S*CH*$_3$), 3.21–3.25 (m, 1H, C*H* of di-n-butyl group)ppm; ^{13}C NMR δ = 14.40, 15.40, 23.12, 23.40, 23.80, 26.34, 26.43, 32.80, 34.22, 34.50, 172.70 ppm; MS: m/z = 248. Analysis: $C_{12}H_{24}OS_2$, Calcd, C, 58.01; H, 9.74; S, 25.81; Obsd: C, 57.73; H, 9.45; S, 26.29.

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