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An Efficient, One-Pot, Triton-B Catalyzed Synthesis of *O*-Alkyl-*S*-methyl Dithiocarbonates^{+}

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Summary. A novel process for the one-step conversion of a variety of primary and secondary alcohols into their *O*-alkyl-*S*-methyl dithiocarbonates using methyl iodide catalyzed by the Triton-B/CS_2 system was developed. Thus, *O*-alkyl-*S*-methyl dithiocarbonates were obtained in very good to excellent yields. This protocol is mild and efficient compared to other methods.

Keywords. Triton-B; Carbon disulfide; Alcohols; Methyl iodide; *O*-Alkyl-*S*-methyl dithiocarbonates.

Introduction

O-Alkyl-*S*-methyl dithiocarbonates (xanthates) are a versatile source of radicals [1], versatile intermediates in the synthesis of thiols [2], thiocarbonates [3], alkenes [4], alkanes [5], S-activated carbanions [6], and photosensitizers [7] for the polymerization of vinyl monomers. They have also been used in the synthesis of natural products [8], *Claisen* rearrangements [9], and are also important for their biological activities [10]. Traditionally, they are prepared from alcohol in a three-step process [11]. The reaction involves the use of strong bases such as sodium hydride, sodium amide, or potassium *t*-butoxide in polar aprotic solvents like *DMSO* [12], *DMF* [13], or *diglyme* [14]. Phase transfer catalysis and crown ethers have also been used with strong bases, specifically for the preparation of dithiocarbonates from unfunctionallized alcohols [15]. 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. Recently, we found that benzyltrimethylammonium hydroxide (Triton-B) is the best reagent for the preparation of carbamates and dithiocarbamates using cheap,

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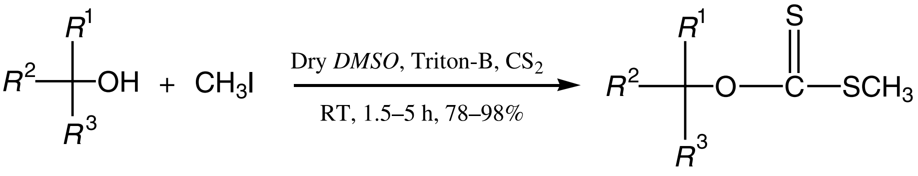
abundantly available, and safe reagents like CO_2 and CS_2 [16]. In the present communication, we report an efficient, one-pot synthesis of *O*-alkyl-*S*-methyl dithiocarbonates from corresponding alcohols and methyl iodide using the Triton-B/CS_2 system.

Results and Discussion

During the course of our recent studies for the synthesis of carbamates and dithiocarbamates, Triton-B has been found to be an efficient and mild basic catalyst [16]. Taking these observations as a guide, we tried a reaction of an alcohol with methyl iodide using the Triton-B/CS_2 system at room temperature. The desired product was isolated and further confirmed by different spectroscopic and analytical techniques. Thus, various alcohols were reacted (Scheme 1) with methyl iodide using the Triton-B/CS_2 system at room temperature for 1.5–5 h yielding *O*-alkyl-*S*-methyl dithiocarbonates in high to excellent yields (70–98%) as shown in Table 1. We tried several solvents like *n*-pentane, *n*-hexane, *n*-heptane, *DMF*, *DMSO,* acetonitrile, *HMPA*, *etc.* and found dry *DMSO* most suitable for good yields of the required products at room temperature.



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Scheme 1

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

Product	R^1	R^2	R^3	Time/h	Yield/%
1a	CH_3	H	H	2.5	90
1b	$CH_3(CH_2)_6$	H	H	2	93
1c	$CH_3(CH_2)_{10}$	H	H	2	95
1d	$CH_3(CH_2)_{14}$	H	H	1.5	98
1e	$(CH_3)_2CHCH_2$	H	H	2.5	92
1f	CH_3	CH_3	H	2.5	85
1g	*Ph*	H	H	2.5	91
1h	$R^1 = R^2 = R^3 = Ph$			3	88
1i	$R^1 = R^2 = R^3 =$ Cyclohexyl			3	82
1j	*Ph*CH=CH	H	H	2.5	80
1k	*Ph*CH_2CH_2	H	H	2.5	94
1l	*Ph*CH_2	CH_3	CH_3	3	92
1m	*n*-C_3H_7	H	H	2	90
1n	$R^1 = R^2 = R^3 =$ Menthyl			4	79
1o	$R^1 = R^2 = R^3 =$ Cholesteryl			5	70
1p	*n*-C_4H_9	*n*-C_4H_9	H	3	78
1q	*n*-C_4H_9	*n*-C_4H_9	*n*-C_4H_9	not formed	

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 the Triton-B/CS_2 system. This reaction generates the corresponding *O*-alkyl-*S*-methyl dithiocarbonates in good to excellent yields. Further, our method exhibits substrate versatility, mild reaction conditions, and experimental convenience. This synthetic protocol is believed to offer a more general method for the formation of C–S bonds, essential for numerous organic syntheses.

Experimental

Chemicals were obtained from Merck, Aldrich, and Fluka. IR spectra were recorded on a Bomem MB-104 FTIR spectrometer and ^{1}H NMRs were scanned on an AC-300F NMR (300 MHz) instrument using $CDCl_3$ as solvent and *TMS* as internal standard. Elemental analyses were made by a Carlo-Erba EA1110 CNNO-S analyzer and agreed favorably with calculated values.

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 min at rt. Triton-B (6 mmol) was added and the reaction was continued at rt for 1 h. Now 6 mmol methyl iodide were added. The reaction was further continued until completion (*cf.* Table 1). The reaction mixture was poured into 50 cm^3 distilled H_2O and extracted with ethyl acetate thrice. The organic layer was separated, dried (Na_2SO_4), and concentrated to give the desired compound.

O-Ethyl-S-methyl dithiocarbonate (**1a**, $C_4H_8OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000{-}2900, 1230, 1065\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 1.40$–1.43 (t, OCH_2CH_3), 2.54–2.57 (s, 3H, SCH_3), 4.54–4.57 (m, 2H, OCH_2CH_3) ppm; MS: $m/z = 136$.

O-Octyl-S-methyl dithiocarbonate (**1b**, $C_{10}H_{20}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000{-}2860, 1231, 1080\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 0.96$–1.56 (m, 15H), 2.52 (s, 3H), 4.55–4.59 (t, 2H) ppm; MS: $m/z = 220$.

O-Dodecyl-S-methyl dithiocarbonate (**1c**, $C_{14}H_{28}OS_2$)
Oil; IR (neat):$\bar{\nu} = 3000{-}2850, 1240, 1082\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 0.94$–1.57 (m, 23H), 2.54 (s, 3H), 4.60–4.63 (t, 2H) ppm; MS: $m/z = 276$.

O-Hexadecyl-S-methyl dithiocarbonate (**1d**, $C_{18}H_{36}OS_2$)
Mp = 28.5°C; IR (KBr): $\bar{\nu} = 3000{-}2855, 1238, 1081\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 0.95$–1.67 (m, 31H), 2.53 (s, 3H), 4.61–4.64 (t, 2H) ppm; MS: $m/z = 332$.

O-(3-Methylbutyl)-S-methyl dithiocarbonate (**1e**, $C_7H_{14}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000{-}2850, 1236, 1079\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 0.96$ (d, 6H), 1.70–1.73 (m, H), 2.53 (s, 3H), 4.60–4.63 (t, 2H) ppm; MS: $m/z = 178$.

O-(1-Methyethyl)-S-methyl dithiocarbonate (**1f**, $C_5H_{10}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000{-}2900, 1238, 1070\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 1.36$ (d, 6H), 2.53 (s, 3H), 5.76–5.79 (m, H) ppm; MS: $m/z = 150$.

O-Phenylmethyl-S-methyl dithiocarbonate (**1g**, $C_9H_{10}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3100{-}2900, 1245, 1084\,cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 2.56$ (s, 3H), 5.62–5.64 (m, 2H) 7.30–7.38 (m, 5H) ppm; MS: $m/z = 198$.

O-Phenyl-S-methyl dithiocarbonate (**1h**, $C_8H_8OS_2$)
Oil; IR (neat): $\bar{\nu} = 3100, 2950, 1600, 1500, 1200, 1060\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.57$ (s, 3H), 7.20–7.25 (m, 5H) ppm; MS: $m/z = 198$.

O-Cyclohexyl-S-methyl dithiocarbonate (**1i**, $C_8H_{14}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000-2850, 1230, 1070\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.44$–1.59 (m, 10H), 2.54 (s, 3H), 5.60 (m, H) ppm; MS: $m/z = 190$.

O-Styryl-S-methyl dithiocarbonate (**1j**, $C_{10}H_{10}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3100, 2940, 1228, 1065\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.55$ (s, 3H), 5.60 (s, H), 6.6 (s, H), 7.15–7.30 (m, 5H) ppm; MS: $m/z = 210$.

O-(3-Phenylpropyl)-S-methyl dithiocarbonate (**1k**, $C_{11}H_{14}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3100-2955, 1232, 1072\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.80$–1.82 (m, 2H), 2.52 (s, 3H), 2.60–2.63 (t, 2H), 3.85–3.90 (t, 2H), 7.08–7.25 (m, 5H) ppm; MS: $m/z = 226$.

O-(1,1-Dimethyl-2-phenylethyl)-S-methyl dithiocarbonate (**1l**, $C_{12}H_{16}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3100-2950, 1234, 1075\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.26$ (s, 6H), 2.54 (s, 3H), 2.66 (s, 2H), 7.10–7.20 (m, 5H) ppm; MS: $m/z = 240$.

O-Butyl-S-methyl dithiocarbonate (**1m**, $C_6H_{12}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000-2900, 1235, 1072\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.93$–0.96 (m, 3H), 1.33–1.48 (m, 4H), 2.54 (s, 3H), 4.20–4.25 (m, 2H, OCH_2) ppm; MS: $m/z = 164$.

O-Menthyl-S-methyl dithiocarbonate (**1n**, $C_{12}H_{22}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000-2950, 1233, 1075\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.85$–0.87 (d, 3H), 0.90–0.95 (d, 6H), 1.15–2.20 (m, 8H), 2.50 (s, 3H), 5.45–5.50 (m, H) ppm; MS: $m/z = 246$.

O-Cholesteryl-S-methyl dithiocarbonate (**1o**, $C_{28}H_{46}OS_2$)
Mp = 125°C; IR (KBr): $\bar{\nu} = 3000-2850, 1241, 1082\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.84$–0.86 (s, 3H), 0.90–0.95 (d, 6H), 1.10 (s, 3H), 1.15 (s, 3H), 1.21–2.20 (m, 31H), 2.54 (s, 3H), 3.50–3.53 (m, H), 5.50–5.55 (m, H) ppm; MS: $m/z = 246$.

O-sec-Butyl-S-methyl dithiocarbonate (**1p**, $C_{10}H_{20}OS_2$)
Oil; IR (neat): $\bar{\nu} = 3000-2950, 1237, 1070\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.93$–0.96 (t, 3H), 1.20–1.23 (d, 3H), 1.60–1.63 (m, 2H), 2.55 (s, 3H), 5.50–5.55 (m, H, CH) ppm; MS: $m/z = 220$.

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