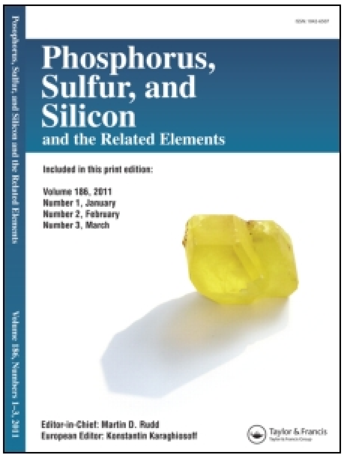

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Superoxide Ion-Promoted Facile One-Pot Synthesis of *O*-Alkyl-*S*-methyl Dithiocarbonates from Alcohol Under Mild Reaction Conditions

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SUPEROXIDE ION–PROMOTED FACILE ONE-POT SYNTHESIS OF *O*-ALKYL-*S*-METHYL DITHIOCARBONATES FROM ALCOHOL UNDER MILD REACTION CONDITIONS

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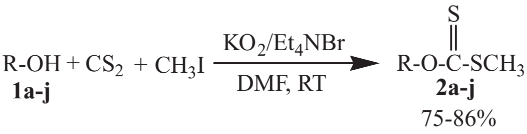
GRAPHICAL ABSTRACT



$$\text{R-OH} + \text{CS}_2 + \text{CH}_3\text{I} \xrightarrow[\text{DMF, RT}]{\text{KO}_2/\text{Et}_4\text{NBr}} \text{R-O-}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{-SCH}_3$$

1a-j **2a-j** 75-86%

Abstract *A new, mild, and efficient protocol for the one-pot synthesis of* O-*alkyl*-S-*methyl dithiocarbonates (xanthates) has been described in reasonably good yields from a variety of alcohols employing carbon disulfide and methyl iodide using superoxide ion at room temperature.*

Keywords Alcohols; dithiocarbonates; phase-transfer catalyst; superoxide ion

INTRODUCTION

O-Alkyl-*S*-methyl dithiocarbonates (xanthates) have attracted a great deal of interest due to their use as a versatile source of radicals,[1] intermediates in organic synthesis,[2–6] and photosensitisers.[7] Their synthetic applications in natural products[8] and Claisen rearrangement[9] are also well documented in the literature. They have also received wide attention due to their marked biological activities.[10] Traditionally, xanthates are prepared from an alcohol in a three-step process.[11] The reaction involves the use of strong bases such as sodium hydride, sodium amide, or potassium *tert*-butoxide in polar aprotic solvents such as DMF,[12] DMSO,[13] or diglyme.[14] Mitsunobu's reagent,[15] Cs_2CO_3-TBAI,[16] and basic resin[17] have also been used for the preparation of dithiocarbonates from different alcohols. Phase-transfer catalysis and crown ethers have also been used with strong bases specifically for the preparation of dithiocarbonates from unfunctionalized alcohols.[18] Recently TBAH-catalyzed, one-pot synthesis of symmetrical trithiocarbonates from alkyl halides and carbon disulfide under neat aqueous conditions has been reported.[19] However, most

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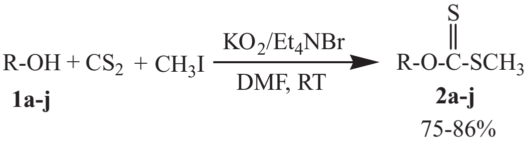
of these methods suffer from limitations such as long reaction times, use of expensive reagents, strongly basic conditions, and tedious workup. Consequently, there is continued interest in developing new and convenient methods for the synthesis of dithiocarbonate using mild reaction conditions.

RESULTS AND DISCUSSION

In light of the above, and as a part of our ongoing research on the use of the superoxide ion[20] in organic synthesis, we report in this article a mild and efficient one-pot synthesis of *O*-alkyl-*S*-methyl dithiocarbonates via a three-component coupling of an alcohol, carbon disulfide, and methyl iodide using in situ–generated tetraethylammonium superoxide in dry DMF at room temperature (Scheme 1).



$$\underset{\textbf{1a-j}}{\text{R-OH}} + CS_2 + CH_3I \xrightarrow[\text{DMF, RT}]{KO_2/Et_4NBr} \underset{\substack{\textbf{2a-j}\\ 75\text{-}86\%}}{\text{R-O-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-SCH}_3}$$

Scheme 1 Superoxide-induced synthesis of dithiocarbonates.

In order to achieve the optimum yield of the product, the effect of various parameters such as molar proportion of the reactants and effect of solvents (DMF, DMSO, and CH_3CN) were investigated in detail using **1c** as a reference compound. The best result was obtained using **1c**, CS_2, methyl iodide, KO_2, and Et_4NBr in the molar proportion 1:1.5:2:2:1 at room temperature in dry DMF in 2.0 h. Under the optimized set of reaction conditions, various alcohols (**1a–j**) were made to undergo smooth coupling with CS_2 and methyl iodide in the presence of tetraethylammonium superoxide (Et_4NO_2) at room temperature to afford *O*-alkyl-*S*-methyl dithiocarbonates in very good yields (75–86%, Table 1).

Tetraethylammonium bromide behaves as an inexpensive phase-transfer catalyst to generate tetraethylammonium superoxide (Et_4NO_2) in the presence of potassium superoxide. Superoxide is assumed to initiate the reaction by proton abstraction from the substrate followed by nucleophilic attack and methylation under significantly mild reaction conditions in aprotic medium.

A comparison of the existing methods for the synthesis of xanthates is described in Table 2.

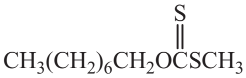
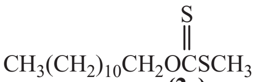
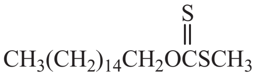
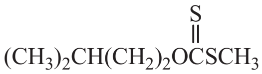
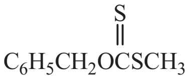
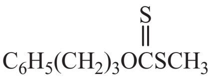
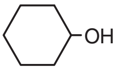
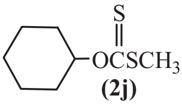
CONCLUSION

In conclusion, a new and mild approach for the one-pot synthesis of *O*-alkyl-*S*-methyl dithiocarbonates has been achieved by using superoxide ion in non-aqueous medium employing alcohols, CS_2, and methyl iodide.

EXPERIMENTAL

Potassium superoxide and tetraethylammonium bromide were purchased from E. Merck, Germany, and were used as received. Dry *N*,*N*-dimethylformamide (DMF) was purchased from Aldrich, USA, and was stored over molecular sieves (4Å) prior to use. The other reagents and solvents were of AR grade. NMR spectra were recorded on a JEOL

Table 1 Et_4NO_2 induced one-pot synthesis of *O*-alkyl-*S*-methyl dithiocarbonates

Entry	Substrate	Product	Time (h)	Yield (%)[a]	Ref.
1	C_4H_9OH (**1a**)	 $C_4H_9O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2a)**	1.75	82	17
2	$CH_3(CH_2)_7OH$ (**1b**)	 $CH_3(CH_2)_6CH_2O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2b)**	2.0	86	18b
3	$CH_3(CH_2)_{11}OH$ (**1c**)	 $CH_3(CH_2)_{10}CH_2O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2c)**	2.0	80	17
4	$CH_3(CH_2)_{15}OH$ (**1d**)	 $CH_3(CH_2)_{14}CH_2O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2d)**	2.0	85	18b
5	$(CH_3)_2CHOH$ (**1e**)	 $(CH_3)_2CHO\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2e)**	1.75	77	18b
6	$(CH_3)_2CH(CH_2)_2OH$ (**1f**)	 $(CH_3)_2CH(CH_2)_2O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2f)**	2.0	83	18b
7	C_6H_5OH (**1g**)	 $C_6H_5O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2g)**	1.5	82	18b
8	$C_6H_5CH_2OH$ (**1h**)	 $C_6H_5CH_2O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2h)**	2.0	81	18b
9	$C_6H_5(CH_2)_3OH$ (**1i**)	 $C_6H_5(CH_2)_3O\overset{\overset{S}{\parallel}}{C}SCH_3$ **(2i)**	2.0	84	17
10	 **(1j)**	 **(2j)**	2.0	75	18b

[a]Isolated yield.

Table 2 Comparison of different methods of synthesizing xanthates

Entry	Bases	Reaction conditions	Time (h)	Yield (%)	Ref.
1.	Pot. *tert*-butoxide	0°C	–	60–65	14
2.	Mitsunobu's reagent	rt	4–8	76–98	15
3.	Cs_2CO_3/TBAI	0°C to rt	3–12	57–96	16
4.	Basic resin	rt	2–6	72–98	17
5.	50% aq. NaOH/nBu_4NHSO_4	rt	0.5–1.5	80–95	18

AL300 FTNMR spectrometer; chemical shifts are given in δ ppm, relative to TMS as internal standard. Crude products were purified using column chromatography.

General Procedure for Synthesis of *O*-Alkyl-*S*-methyl Dithiocarbonates (2a–j)

A mixture of potassium superoxide (0.568 g, 8 mmol) and tetraethylammonium bromide (0.840 g, 4 mmol) (weighed under a nitrogen atmosphere using an atmosbag) in dry DMF (20 mL) was stirred for 15 min and then CS_2 (0.457 g, 6 mmol) was added while continuing the stirring. After 10 min, the alcohols **1** (4 mmol) and methyl iodide (1.14 g, 8 mmol) were introduced, and the stirring was continued. After the reaction was over (1.5 to 2 h, TLC), cold brine solution (10 mL) was added to decompose the unreacted potassium superoxide. The mixture was then extracted with diethyl ether (3 × 15 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated to give the product **2**, which was purified by column chromatography.

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