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An efficient one-pot Michael addition of dithiocarbamate anion to α,β-unsaturated olefins mediated by lithium perchlorate

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RESEARCH ARTICLE

An efficient one-pot Michael addition of dithiocarbamate anion to α,β-unsaturated olefins mediated by lithium perchlorate

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The reaction of substituted dithiocarbamates with electrophilic alkenes in the presence of $LiClO_4$ was investigated in an attempt to prepare numerous ethyl dithiocarbamates bearing β-electron-withdrawing-group substituents. The reaction conditions are mild, neutral, with extremely simple work-up procedures, and offer high yield.

Keywords: Michael addition; Carbon disulfide; Lithium perchlorate; α,β-Unsaturated olefins

1. Introduction

It is well known that dithiocarbamate derivatives have various applications in organic synthesis [1–7], serving as protecting groups [8, 9], as donor ligands [10], or as intermediates for further synthesis [11]. Also, different transition metal complexes of dithiocarbamates have been synthesized for various studies, primarily because of their applications as organic superconductors [12–15].

The reported procedures for the preparation of dithiocarbamates are limited, as common protocols include the use of costly and toxic reagents such as thiophosgene and isothiocyanate [16, 17]. Recently several methods for the preparation of dithiocarbamate derivatives from CS_2 have been published, using bases such as NaOH, $NaOC_2H_5$, K_3PO_4, Et_3N, Cs_2CO_3, and guanidine [18–26].

Buess reported a Michael-type reaction of dithiocarbamates with acrylamide in the presence of triethylamine [21]. In addition, Guo used K_3PO_4 as the base for the conjugate addition of an amine and carbon disulfide to α,β-unsaturated olefins [20].

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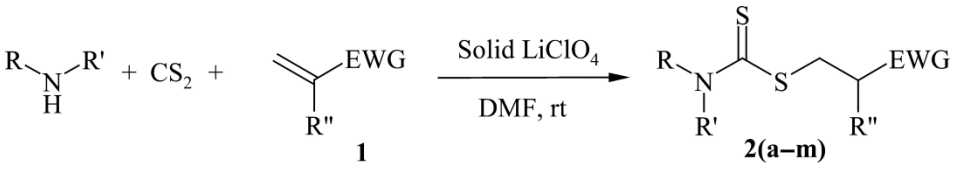


R" = H or Me

SCHEME 1

2. Results and discussion

In connection with our ongoing interest pertaining to the use of solid lithium perchlorate for different organic transformations [27–31], we now wish to report a simple, neutral, and effective one-pot procedure for a Michael addition of the dithiocarbamate anion to α,β-unsaturated olefins mediated by solid lithium perchlorate. This is the first report of the *in-situ* preparation of dithiocarbamate without the use of a strong base (scheme 1, table 1). The reaction is accelerated in the presence of $LiClO_4$, presumably due to the Lewis acidity of lithium ions and the high polarity of the medium. The mild reaction conditions prevent the formation of any undesired by-products. All reactions were carried out at room temperature and in most cases with moderate to high product yields.

Table 1 shows that primary or secondary amines can react with carbon disulfide and different kinds of α,β-unsaturated olefins to give the corresponding β-EWG-substituted ethyl dithiocarbamates. This reaction also works well with different electron-withdrawing groups (EWG), such as –CN, $–C(O)NH_2$, $–CO_2Me$, and $–C(O)CH_3$. The reactions were carried out in one pot and were complete within about 1 h. However, when hindered α,β-unsaturated carbonyl compounds with methyl or methylene groups at the β-position were used, low yields of the products were obtained (entries 14 and 15).

In conclusion, a simple, neutral, and effective method for the preparation of β-electron-withdrawing-group-substituted ethyl dithiocarbamates was developed using solid $LiClO_4$, and without the requirement of a strong base. Therefore, this procedure can serve as a new method for the preparation of substituted ethyl dithiocarbamates.

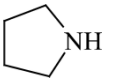
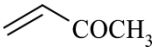
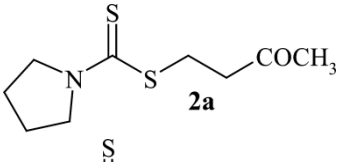
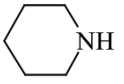
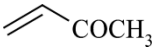
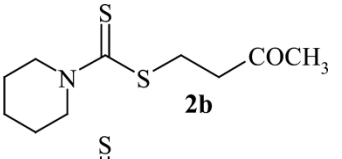
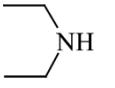
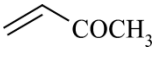
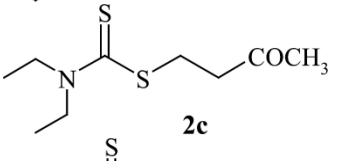
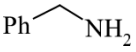
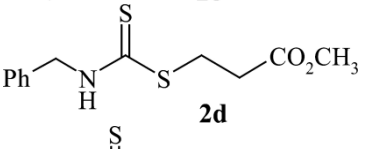
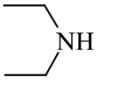
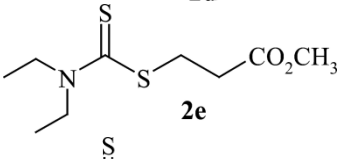
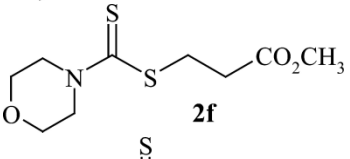
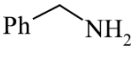
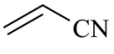
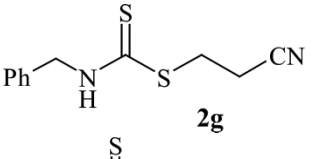
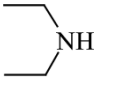
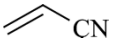
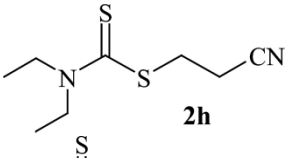
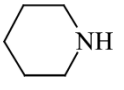
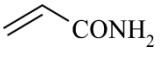
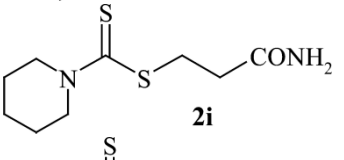
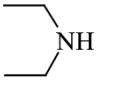
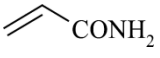
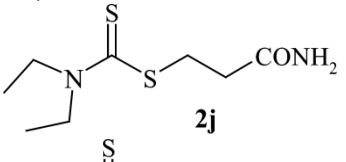
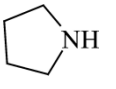
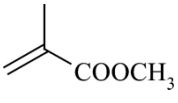
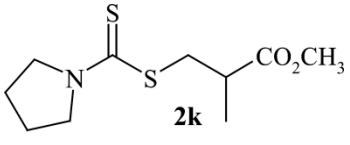
3. Experimental

Reactions were carried out under an atmosphere of argon. NMR spectra were recorded on a Bruker ACF 500 using $CDCl_3$ as solvent. IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer, using samples as KBr discs. Column chromatography was performed using silica gel, Merck grade 60. CH_2Cl_2 or diethyl ether was distilled prior to use. Lithium perchlorate was purchased from Acros Organics. Other chemicals were purchased from Fluka or Merck and were used without further purification. Light petroleum refers to the fraction with distillation range 60–80 °C.

3.1 *General procedure*

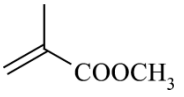
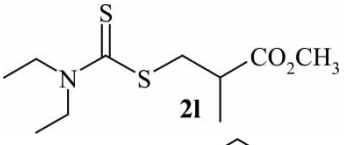
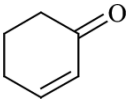
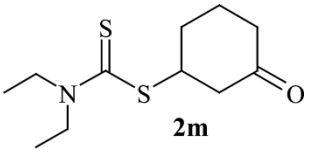
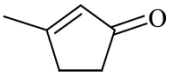
To a stirred solution of an amine (3 mmol) in anhydrous DMF (5 mL) were slowly added carbon disulfide (8 mmol, 0.6 g) and solid $LiClO_4$ (4 mmol, 0.43 g) at room temperature. Then the mixture was stirred for 0.5 h, at which point an α,β-unsaturated olefin (3 mmol) was added over a period of 5 min. The reaction mixture was stirred under argon for 0.5–1 h at room temperature

Table 1. Michael addition of dithiocarbamate anion to α,β-unsaturated olefins.

Entry	Amine	Olefin	Product	Yield (%)[a]
1			 **2a**	85
2			 **2b**	83
3			 **2c**	87
4			 **2d**	89
5			 **2e**	92
6			 **2f**	85
7			 **2g**	89
8			 **2h**	95
9			 **2i**	90
10			 **2j**	90
11			 **2k**	70[b]

(*continued*)

Table 1. Continued.

Entry	Amine	Olefin	Product	Yield (%)[a]
12			 **2l**	75[b]
13			 **2m**	50[b]
14				No reaction[c]

[a]Isolated yields for **2a**–**2l** [20]; [b]After 1.5 h; [c]After 5 h.

and the reaction was monitored by TLC. After completion of the reaction, the solution was poured into water and the organic materials were extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed using a rotary evaporator. Flash chromatography of the residue using silica gel (gradient elution, light petroleum ether–ethyl acetate, 9:1 v/v) afforded the pure product.

3.2 *Data for dithiocarbamates*

Compound 2a. IR υ (cm^{-1}) 1710 (C=O), 1220 (C=S); ^{1}H NMR (CD_3NO_2) δ (ppm) 2.06 (2H, t, $J = 7.2$ Hz), 2.18 (2H, t, $J = 7.2$ Hz), 2.21 (3H, s), 2.94 (2H, t, $J = 7.1$ Hz), 3.43 (2H, t, $J = 7.1$ Hz), 3.69 (2H, t, $J = 7.2$ Hz), 3.89 (2H, t, $J = 7.2$ Hz).

Compound 2b. IR υ (cm^{-1}) 1708 (C=O), 1210 (C=S); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.6 (6H, m), 2.05 (3H, s), 2.82 (2H, t, $J = 7.2$ Hz), 3.35 (2H, t, $J = 7.2$ Hz), 3.78 (2H, br, CH_2N), 4.16 (2H, br, CH_2N).

Compound 2c. IR υ (cm^{-1}) 1710 (C=O), 1225 (C=S); ^{1}H NMR (C_6D_6) δ (ppm) 1.02 (3H, t, $J = 7.0$ Hz), 1.13 (3H, t, $J = 7.0$ Hz), 1.80 (3H, s), 2.71 (2H, t, $J = 7.0$ Hz), 3.39 (2H, br, CH_2N), 3.55 (2H, t, $J = 7.0$ Hz, SCH_2), 3.84 (2H, br, CH_2N).

Compound 2d. IR υ (cm^{-1}) 1735 (C=O), 1215 (C=S); ^{1}H NMR (CD_3NO_2) δ (ppm) 2.82 (2H, t, $J = 7.1$ Hz), 3.53 (2H, t, $J = 7.1$ Hz), 3.73 (3H, s), 4.97 (2H, d, $J = 4.8$ Hz, CH_2NH), 7.40 (5H, m), 7.14 and 8.04 (each 1H, br, together NH and SH).

Compound 2e. IR υ (cm^{-1}) 1730 (C=O), 1205 (C=S); ^{1}H NMR (C_6D_6) δ (ppm) 0.99 (3H, t, $J = 7.2$ Hz), 1.08 (3H, t, $J = 7.2$ Hz), 2.79 (2H, t, $J = 7.1$ Hz), 3.27 (2H, br, CH_2N), 3.40 (3H, s), 3.70 (2H, t, $J = 7.1$ Hz, SCH_2), 3.84 (2H, br, CH_2N).

Compound 2f. IR υ (cm^{-1}) 1735 (C=O), 1210 (C=S); ^1H NMR (C_6D_6) δ (ppm) 2.73 (2H, t, $J = 6.8$ Hz), 3.36 (5H, br, CH_2N and OCH_3), 3.51 (4H, s, CH_2OCH_2), 3.59 (4H, m, CH_2N and SCH_2).

Compound 2g. IR υ (cm^{-1}) 2251, 1203, 747; ^1H NMR (acetone-d_6) δ (ppm) 2.89 (2H, t, $J = 7.1$ Hz, CH_2CN), 3.55 (2H, t, $J = 7.1$ Hz, SCH_2), 4.95 (2H, d, $J = 5$ Hz, CH_2NH), 7.34 (5H, m), 7.15 and 9.48 (each 1H, br, together NH and SH).

Compound 2h. IR υ (cm^{-1}) 2248, 1203; ^1H NMR (C_6D_6) δ (ppm) 1.03 (3H, t, $J = 7.1$ Hz), 1.11 (3H, t, $J = 7.1$ Hz), 2.41 (2H, t, $J = 7.0$ Hz, CH_2CN), 3.17 (2H, $J = 7.0$, SCH_2), 3.35 (2H, q, $J = 7.1$ Hz, CH_2N), 3.77 (2H, q, $J = 7.1$ Hz, CH_2N).

Compound 2i. IR υ (cm^{-1}) 3358, 1646, 1222; ^1H NMR (CD_3NO_2) δ (ppm) 1.78 (6H, br), 2.70 (2H, t, $J = 7.2$ Hz), 3.54 (2H, t, $J = 7.2$ Hz, SCH_2), 3.96 (2H, br, CH_2N), 4.31 (2H, br, CH_2N), 6.0 and 6.33 (together 2H, br, NH_2).

Compound 2j. IR υ (cm^{-1}) 3380, 1653, 1201; ^1H NMR (C_6D_6) δ (ppm) 1.01 (3H, t, $J = 7.2$ Hz), 1.11 (3H, t, $J = 7.2$ Hz), 2.46 (2H, t, $J = 7.2$ Hz), 3.38 (2H, t, $J = 7.2$ Hz, SCH_2), 3.60 (2H, q, $J = 7.2$ Hz, CH_2N), 3.81 (2H, q, $J = 7.2$ Hz, CH_2N), 4.88 and 5.78 (together 2H, br, NH_2).

Compound 2k. IR υ (cm^{-1}) 1730, 1205; ^1H NMR (C_6D_6) δ (ppm) 1.28 (3H, d, $J = 7.2$ Hz), 1.88–2.00 (4H, m), 2.81 (1H, m, CHCO), 3.38 (1H, d, $J = 7.0$ Hz, SCH_2), 3.46 (1H, d, $J = 7.0$ Hz, SCH_2), 3.59 (2H, t, $J = 7.2$ Hz, CH_2N), 3.63 (3H, s, OCH_3), 3.83 (2H, t, $J = 7.2$ Hz, CH_2N).

Compound 2l. IR υ (cm^{-1}) 1735, 1210; ^1H NMR (C_6D_6) δ (ppm) 1.10 (6H, br), 1.28 (3H, d, $J = 7.2$ Hz), 3.00 (1H, m), 3.34 (1H, d, $J = 7.2$ Hz, SCH_2), 3.46 (1H, d, $J = 7.2$ Hz, SCH_2), 3.53 (2H, q, $J = 7.2$ Hz, CH_2N), 3.63 (3H, s), 3.78 (2H, q, $J = 7.2$ Hz, CH_2N).

Compound 2m. IR υ (cm^{-1}) 1715, 1210; ^1H NMR (C_6D_6) δ (ppm) 1.23 (6H, t, $J = 7.2$ Hz), 1.82–2.7 (8H, m), 3.66 (2H, q, $J = 7.2$ Hz, CH_2N), 3.92 (2H, q, $J = 7.2$ Hz, CH_2N), 4.20 (1H, m, SCH).

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