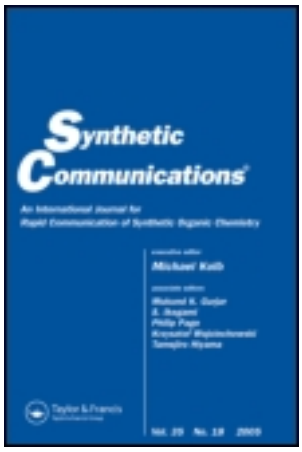

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CONJUGATED ADDITION REACTION OF AMINE, CARBON DISULFIDE TO ELECTROPHILIC ALKENES IN THE PRESENCE OF ANHYDROUS POTASSIUM PHOSPHATE

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CONJUGATED ADDITION REACTION OF AMINE, CARBON DISULFIDE TO ELECTROPHILIC ALKENES IN THE PRESENCE OF ANHYDROUS POTASSIUM PHOSPHATE

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ABSTRACT

Different kinds of β-electron-withdraw group substituted ethyl dithiocarbamates (**3**) were prepared by the conjugated addition of an amine (**1**) and carbon disulfide to electrophilic alkenes (**2**) in the presence of anhydrous potassium phosphate under mild condition in good yields.

In the previous papers,[1–4] we have reported an efficient one-pot method for the preparation of dithiocarbamate by the reaction of an amine and carbon disulfide with alkyl halide in the presence of anhydrous potassium phosphate. The anhydrous potassium phosphate plays an important part in this method. As an extension of this method, we were interested to explore the

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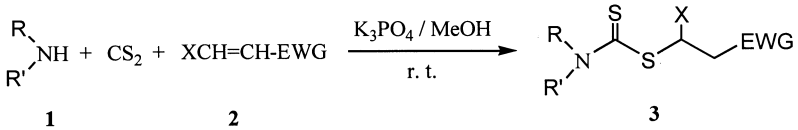
application of anhydrous potassium phosphate in the conjugated addition reaction of an amine and carbon disulfide to electrophilic alkenes to form β-electron-withdrawing group substituted ethyl dithiocarbamates in this paper.

Two methods for the preparation of β-electron-withdrawing group substituted ethyl dithiocarbamates have been reported.[5–7] Our results were listed in Table 1. The structures of **3a–j** conformed to "lectures" report and the data of IR and ^{1}H NMR were listed in Table 2. It can be found from

Table 1. Synthesis of Compounds **3**



1 **2** **3**

Compd.	RR'N-	XCH=CH-EWG	mp(Lit) °C	Yield(Lit.) %
3a	Et_2N-	CH_2=CHCN	yellow oil	83 (91[8])
3b		CH_2=CHCN	79.5-80.5 (79-80[8])	88 (78[8])
3c	n-BuNH-	CH_2=CHCN	50-52 (52-53[8])	90 (89[8])
3d	$PhCH_2NH$-	CH_2=CHCN	54-55 (54[6])	86
3e		CH_2=CHCN	142-143 (140[5])	91
3f	Et_2N-	CH_2=$CHCONH_2$	107-108 (108-109[7])	64 (84[7])
3g		CH_2=$CHCONH_2$	117-118 (115-117[7])	70 (82[7])
3h	Et_2N-	CH_2=$CHCO_2Et$	yellow oil	65
3i		CH_2=$CHCO_2Et$	45-46 (46-47.5[8])	66
3j		PhCH=$CHNO_2$	87-88 (88-89[7])	97 (90[7])

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Table 2. IR and ^{1}H NMR Data of Compounds **3a–j**

Compd.	IR (KBr or film) ν (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS, δ)
3a	2248 1203	1.28 (6H, t, J = 7.2, CH_3), 2.88 (2H, t, J = 5.4, CH_2CN), 3.53 (2H, t, J = 5.4, -SCH_2), 3.73 (2H, q, J = 7.2, -CH_2N-), 4.00 (2H, q, J = 7.2, -CH_2N-)
3b	2249 1228	1.72 (6H, br, -$(CH_2)_3$-), 2.89 (2H, t, J = 6.6, CH_2CN), 3.55 (2H, t, J = 6.6, -SCH_2), 3.88 (2H, br, -CH_2N-), 4.28 (2H, br, -CH_2N-)
3c	3359 2249 1199	0.98 (3H, t, J = 7.2, CH_3), 1.37 (2H, m, $CH_3\underline{CH_2}$-), 1.56 (2H, m, -$\underline{CH_2}CH_2N$-), 2.90 (2H, t, J = 6.6, CH_2CN), 3.47 (2H, t, J = 6.6, -SCH_2), 3.60 (1H, m, CH_2N-), 4.08 (1H, m, CH_2N-), 5.54, 5.81 (1H, 2br, -NH and -SH)
3d	2251 1203 747	2.90 (2H, t, J = 6.6, CH_2CN), 3.53 (2H, t, J = 6.6, -SCH_2), 4.60 (2/5H, d, J = 4.8, -CH_2NCS-), 4.28 (8/5H, d, J = 5.4, -CH_2NC (=SH)S-), 7.16, 7.76 (1H, 2br, -NH and -SH), 7.34 (5H, m, Ar)
3e	2241 1201	2.90 (4H, t, J = 6.6, CH_2CN), 3.58 (4H, t, J = 6.6, -SCH_2), 4.08 (4H, br, pip), 4.42 (4H, br, pip)
3f	3386 1653 1201	1.28 (6H, t, J = 7.2, CH_3), 2.71 (2H, t, J = 6.9, CH_2CO-), 3.59 (2H, t, J = 6.9, -SCH_2), 3.72 (2H, q, J = 7.2, -CH_2N-), 4.04 (2H, q, J = 7.2, -CH_2N-), 5.55 (1H, br, -NH), 5.78 (1H, br, -NH)
3g	3358 1646 1222	1.70 (6H, br, -$(CH_2)_3$-), 2.71 (2H, t, J = 6.9, CH_2CO-), 3.60 (2H, t, J = 6.9, -SCH_2), 3.88 (2H, br, -CH_2N-), 4.29 (2H, br, -CH_2N-), 5.75 (2H, br, -NH_2)
3h	1730 1205	1.28 (9H, m, $3 \times CH_3$), 2.79 (2H, t, J = 6.6, CH_2CO-), 3.56 (2H, t, J = 6.6, -SCH_2), 3.72 (2H, q, J = 6.9, -CH_2N-), 4.04 (2H, q, J = 7.2, -CH_2N-), 4.15 (2H, q, J = 7.2, $CH_3\underline{CH_2}$-)
3i	1725 1229	1.28 (3H, t, J = 7.2, -CH_3), 1.70 (6H, br, -$(CH_2)_3$-), 2.80 (2H, t, J = 6.9, CH_2CO-), 3.58 (2H, t, J = 6.9, -SCH_2), 3.87 (2H, br, -CH_2N-), 4.15 (2H, q, J = 7.2, -$\underline{CH_2}CH_3$), 4.28 (2H, br, -CH_2N-)
3j	1550 1225 744	1.68 (6H, br, -$(CH_2)_3$-), 3.81 (2H, br, -CH_2N-), 4.18, 4.32 (2H, 2br, -CH_2N-), 4.87 (1H, dd, J = 10.5, 13.2, -SCH-), 5.34 (1H, dd, J = 13.5, 4.8, -$CHNO_2$), 5.74 (1H, dd, J = 13.5, 4.8, -$CHNO_2$), 7.33 (5H, m, Ar)

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Table 1 that in the presence of anhydrous potassium phosphate, primary or secondary amine (**1**) can react easily with carbon disulfide and different kinds of electrophilic alkenes (**2**) to give corresponding β-electron-withdrawing group substituted ethyl dithiocarbamates (**3**) at room temperature in good yield. The reaction was carried out at one-pot and most of the reactions were completed within 0.5 to 4 h. The electron-withdrawing groups **Y** of electrophilic alkenes (**3**) can be -CN, $-CO_2Et$, $-CONH_2$ or $-NO_2$ and the X of electrophilic alkenes (**3**) can be hydrogen or aromatic group. When the $CH_3CH{=}CHCHO$, $CH_3CH{=}CHCO_2Et$, $CH_2{=}CCH_3CO_2Et$ or $PhCH{=}CHCOCH_3$ was used as electrophilic alkenes, the reaction was difficult. The high steric effect may be the main reason.

In conclusion, a new one-pot synthetic method for the β-electron-withdrawing group substituted ethyl dithiocarbamates was found.

EXPERIMENTAL

Melting points were determined on X4 microscope and were uncorrected. IR spectra were recorded on Perkin-Elmer 298 instrument (KBr disk or liquid film). ^{1}H NMR spectra were performed on a VXR 300 (300 MHz) instrument in $DCCl_3$. Thin layer chromatography was carried out on pre-coated GF_{254} silica gel plates. The column chromatography was performed using G60 H silica gel. Anhydrous potassium phosphate was obtained from dehydration of $H_3PO_4{\cdot}7H_2O$. The other reagents and solvents were of commercial quality from freshly opened containers.

General procedure. To a stirred solution of amine **1** (3 mmol) and anhydrous potassium phosphate (0.64 g, 3 mmol) in methanol (15 mL) was added carbon disulfide (20 drops, ~9 mmol) at $< 10^{\circ}$C. After the mixture was stirred at this temperature for 0.5 h, the electrophilic alkene **2** (3 mmol) was added. Then the reaction was continued at room temperature and was monitored by TLC (GF_{254}, petroleum ether–ethyl acetate). At the completion of the reaction, the precipitate was filtered off. Evaporation of the solvent and flash chromatography of the residue on silica gel (gradient elution, petroleum ether–ethyl acetate) afforded pure target compound **3**.

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