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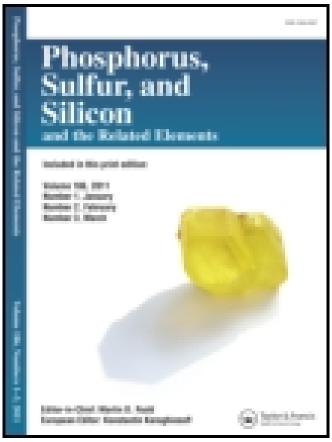

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OH^-/Silica-Mediated One-Pot Synthesis of Dithiocarbamates Under Solvent-Free Conditions

Ghasem Rezanejade Bardajee [a], Hamid Samareh Afsari [a], Seyediraj Sadraei [a] & Seyedehmaryamdokht Taimoory [a]
[a] Department of Chemistry, Payame Noor University, Tehran, Islamic Republic of Iran

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OH⁻/SILICA-MEDIATED ONE-POT SYNTHESIS OF DITHIOCARBAMATES UNDER SOLVENT-FREE CONDITIONS

Ghasem Rezanejade Bardajee, Hamid Samareh Afsari, Seyediraj Sadraei, and Seyedehmaryamdokht Taimoory
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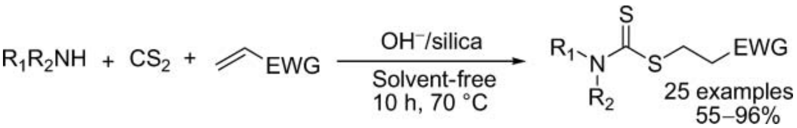
GRAPHICAL ABSTRACT



Abstract *An efficient, versatile, and environmentally benign method for the synthesis of dithiocarbamates under solvent-free conditions is reported. The Michael addition of electron-deficient alkenes with alkyl or aryl amines and CS_2 in the presence of OH^-/silica in a one-pot three-component reaction protocol gave the corresponding dithiocarbamates in good to excellent yields. This method is suitable for a wide range of amines and a variety of Michael acceptors in solvent-free conditions. The results of the present work show the desired products in excellent yields.*

Keywords Dithiocarbamates; OH^-/silica; amines; solvent-free; electron-deficient alkenes

INTRODUCTION

Carbon–sulfur bond formation is a fundamental approach to bring sulfur into organic compounds, and this has received much attention due to its occurrence in many molecules that are of biological and pharmaceutical importance.[1,2] Organic dithiocarbamates, ubiquitously found in a variety of biologically active molecules,[3] are of high importance in academia as well as in industry.[4] Besides being widely used as fungicides to protect crops from fungal diseases,[5] dithiocarbamic acid esters have a number of other applications such as in photochemistry,[6] as catalyst in the sulfur vulcanization of rubber,[7] and numerous biological and medicinal properties including applications in the treatment of cancer,[8] play pivotal roles in agriculture,[9] and act as linkers in solid-phase organic synthesis.[10] They are

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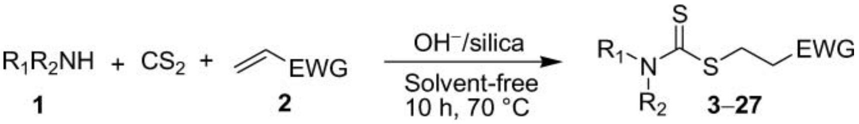
Address correspondence to Ghasem Rezanejade Bardajee, Department of Chemistry, Payame Noor University 19395-4697, Tehran, Islamic Republic of Iran. E-mail: rezanejad@pnu.ac.ir

used in controlled radical polymerization techniques,[11,12] and recently, in the synthesis of ionic liquids.[13] For these reasons, the synthesis of functionalized dithiocarbamates using different substitution patterns at the thiol chain has become a field of increasing interest in synthetic organic chemistry during the past few years. In the past, dithiocarbamic acid esters had been prepared from the reaction of amines with expensive and toxic reagents, such as thiophosgene and isothiocyanate.[14,15] Because of some limitations such as long reaction times, low product yields, or harsh reaction conditions, researchers are still attempting to improve the preparation methods of dithiocarbamates. Recently, a one-pot reaction of amines with carbon disulfide (CS_2) and electrophilic reagents has been developed. Much effort has been focused on the exploration of reaction conditions for one-pot preparation of these compounds.[15–18] Various bases, for instance, $NaOC_2H_5$, Et_3N, Cs_2CO_3, and guanidine as well as different solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and methanol have been used to catalyze or improve the reaction performance. However, it is still a challenge to synthesize aryldithiocarbamic acid esters from aryl amines, because few previous reports used aryl amines as low reactivity substrates to participate in the synthesis of dithiocarbamates through Michael addition reactions.[18]

OH^-/silica is a basic support, which is simply prepared from easily available, cheap, and commercial starting materials.[19] Owing to the basic nature of this support, it can be considered as a good replacement for organic bases in various reactions. For example, this catalyst was applied for the transesterification of refined sunflower oil with methanol at 323 K and atmospheric pressure.[19] Herein, we describe an efficient synthesis of aryl and also alkyl dithiocarbamic acid esters from solvent-free reaction of aryl and alkyl amines, CS_2, and electrophilic alkenes in the presence of OH^-/silica as outlined in Scheme 1.



Scheme 1

RESULTS AND DISCUSSION

Herein, our contribution is intended to extend the scope of available methods for the synthesis of dithiocarbamates via description of the use of OH^-/silica as a new support in their synthesis. Our investigations show that the Michael reaction of benzylamine with CS_2 and acrylonitrile in the presence of OH^-/silica under solvent-free conditions affords the corresponding dithiocarbamates in good yields (Scheme 1). This result developed our interest in an efficient procedure for the synthesis of alkyl and aryldithiocarbamates.

To test the feasibility of this reaction, we initially investigated the Michael reaction of benzylamine with CS_2 and acrylonitrile under various reaction conditions. To this end, solvents such as diethylether, DMF, acetonitrile, and dichloromethane as well as a solvent-free medium were tested as the reaction medium. Because of the high yields and green protocol, solvent-free conditions were found to be the best for this reaction (Table 1, entries 1–5). In the next step, the amount of OH^-/silica was changed in the reaction to find the optimum amount of support with respect to the yield of the reaction (Table 1, entries 4, 6–8). The overall yield versus a variation in temperature up to 100 °C was also investigated.

Table 1 Screening of the conditions for the Michael reaction of benzylamine with CS_2 and acrylonitrile in the presence of OH^-/silica[a]

Entry	Solvent	OH^-/silica (g)	Temperature (°C)	Yield (%)[b]
1	Diethylether	0.1	r.t.	25
2	DMF	0.1	r.t.	48
3	Acetonitrile	0.1	r.t.	42
4	Solvent-free	0.1	r.t.	64
5	Dichloromethane	0.1	r.t.	25
6	Solvent-free	0.05	r.t.	45
7	Solvent-free	0.15	r.t.	64
8	Solvent-free	0.2	r.t.	64
9	Solvent-free	0.1	50	71
10	Solvent-free	0.1	70	85 (81)[c]
11	Solvent-free	0.1	100	85

Note: r.t., room temperature.

[a] All reactions were run under the following conditions: benzylamine (1 mmol), CS2 (1 mmol), acrylonitrile (1 mmol), and OH-/silica (0.05–0.2 g) in the preferred solvent (2 mL) were heated in a sealed tube at the desired temperature for 10 h.

[b] GC yields.

[c] Isolated yield in parentheses.

The desired product was obtained in 85% GC yield in a solvent-free green reaction medium at 70 °C (81% isolated yield, Table 1, entry 10).

Having established the optimum reaction conditions, we next examined the generality of these conditions to other substrates using several alkyl or aryl amines and electron-deficient alkenes. As shown in Table 2, the aliphatic amines including primary amines and acyclic or cyclic secondary amines could afford the corresponding products in high yields when reacted with a variety of Michael acceptors such as methyl acrylate, acrylonitrile, and acrylamide (Table 2, entries 1–19). The reactivity of alkyl amines was mainly controlled by steric and electronic effects. For example, *tert*-butylamine showed lower yields compared with other primary and secondary amines (Table 2, entry 8) due to its steric effect. The reaction of cyclic secondary amines such as pyrolidine took place in higher yields compared with the other amines (Table 2, entries 15–18). This higher reactivity can be attributed to the nucleophilicity of cyclic secondary amines versus other steric factors. Furthermore, the nature of a Michael acceptor can influence the performance of the reaction. For instance, by using acrylonitrile or methyl acrylate as a Michael acceptor, all tested alkyl and aryl amines gave the expected products in good to excellent yields (Table 2, entries 17–25), while the use of acrylamide as a Michael acceptor resulted in moderate yields (Table 2, entry 16). The dominant mechanism for the production of dithiocarbamates can be summarized by a nucleophilic addition of amine to CS_2 followed by the Michael addition of the corresponding thiolate anion to electron-deficient alkenes. We believe that the basic nature of OH^-/silica activates nucleophilic amine groups to attack the desired electrophilic substrates such as CS_2 or electron-deficient alkenes.[20]

We also examined the reusability of OH^-/silica. The reusability of supported catalysts is an important benefit and makes them useful for commercial applications. We found that the support could be separated and reused after washing with dichloromethane and drying at 90 °C. The results show that the catalyst can be used effectively three times without any loss of its activity (Table 2, entry 5).

Table 2 Dithiocarbamates obtained from the Michael reaction of electron-deficient alkenes with alkyl and aryl amines and CS_2 in the presence of OH^-/silica

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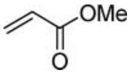
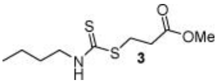
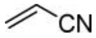
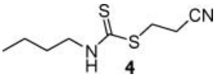
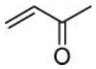
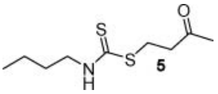
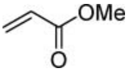
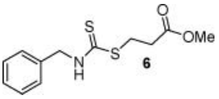
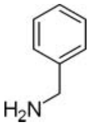
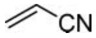
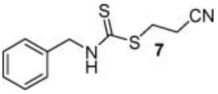
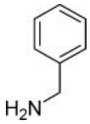
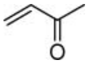
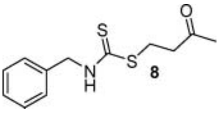
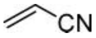
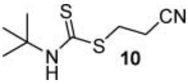
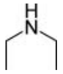
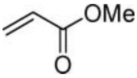
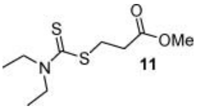
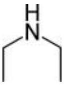
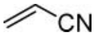
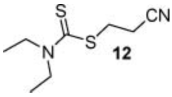
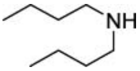
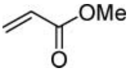
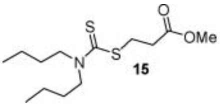
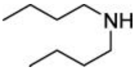
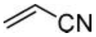
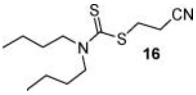
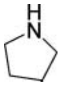
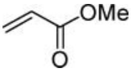
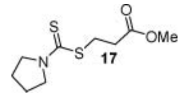
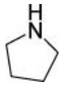
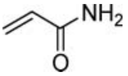
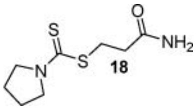
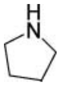
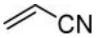
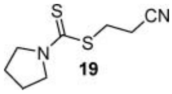
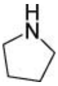
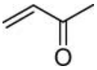
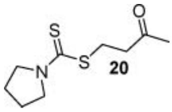
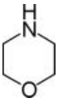
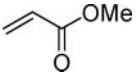
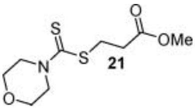
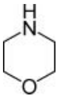
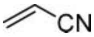
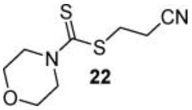
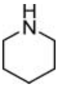
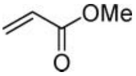
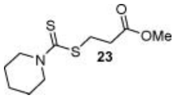
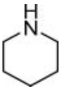
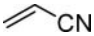
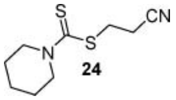
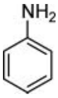
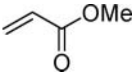
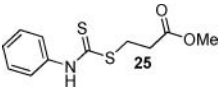
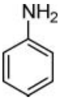
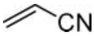
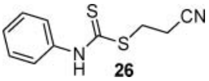
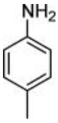
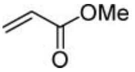
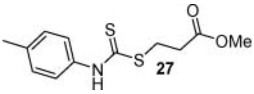
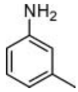
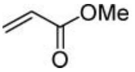
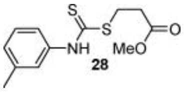
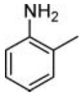
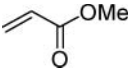
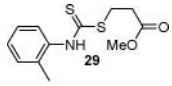
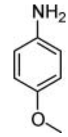
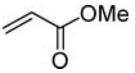
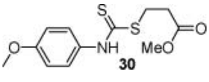
1			 3	91	17
2			 4	82	17
3			 5	76	17
4			 6	93	17, 18
5			 7	81 (75)[c]	17, 18
6			 8	78	17
8			 10	65	17
9			 11	92	17
10			 12	86	17
13			 15	86	17, 18
14			 16	83	17, 18
15			 17	96	17, 18
16			 18	60	17
17			 19	92	17, 18

Table 2 Dithiocarbamates obtained from the Michael reaction of electron-deficient alkenes with alkyl and aryl amines and CS_2 in the presence of OH^-/silica *(Continued)*

Entry	Amine **1**	Compound **2**	Product	Yield (%)[a,b]	Reference
18			 20	84	17
19			 21	92	17
20			 22	81	17
21			 23	88	17
22			 24	82	17
23			 25	78	18
24			 26	55	18
25			 27	84	18
26			 28	71	18
27			 29	66	18
28			 30	80	18

[a] Isolated yields.

[b] All reactions were run under the following conditions: benzylamine (1 mmol), CS_2 (1 mmol), Michael acceptor (1 mmol), and OH^-/silica (0.1 g) were heated in a sealed tube at 70 °C for 10 h.

[c] Isolated yield after three times recycling.

Table 3 Comparison of our results with some previously reported data for the synthesis of dithiocarbamate **6**

Catalyst	Alkyl/aryl amine applicability	Temperature (°C)	Time (h)	Yield (%)	Reference
No catalyst (in water)	Only alkyl amines	r.t.	5–18	80	17
Alkaline Al_2O_3	Alkyl/aryl amines	r.t.	10–30	80	18
OH^-/silica	Alkyl/aryl amines	70	0.5–10	93	This work

Note: r.t., room temperature.

The results show the wide applicability of the presented method. Some previously reported data for the synthesis of dithiocarbamate **6** (Table 2, entry 4) were compared with our results in terms of the applicability to alkyl and aryl amines, temperature, reaction time, and percentage yields (Table 3). As one can see, our results show a very good comparability with previously reported data with respect to yields, applicability, and reaction times.

CONCLUSIONS

In summary, we have described a one-pot, efficient, and novel method for the preparation of dithiocarbamic acid esters by the Michael addition of amines and CS_2 to electron-deficient alkenes in OH^-/silica media. OH^-/silica is an environmentally friendly and recyclable catalyst, which demonstrated to be an excellent catalyst for the reaction. A wide range of amines, especially aryl amines, reacted with CS_2 and an array of Michael acceptors to afford the Michael addition products in high yields. Furthermore, the procedure offers several advantages including cleaner reactions, improved yields, and simple experimental procedures, which make it a useful and attractive strategy in multicomponent reactions in combinatorial chemistry.

EXPERIMENTAL

Materials

All amines, Michael acceptors, CS_2, and solvents were commercially available and were purchased from Merck or Sigma-Aldrich and used without further purification. The solvents were analytical grade and used as received. The course of the syntheses was followed by thin layer chromatography on silica gel plates (Merck, silica gel 60 F_{254}, ready to use), using ethyl acetate:*n*-hexane (1:3) as eluent.

Instrumentation

^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 500 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as the NMR solvents. ^1H NMR spectra are referenced to tetramethylsilane (0.00 ppm) and ^{13}C NMR spectra are referenced from the solvent central peak (e.g., 77.23 ppm for $CDCl_3$). Chemical shifts are given in ppm. Gas chromatography-mass spectrometry (electron impact) [GC-MS (EI)], 70 eV, and HP 6890 column: HP-5 (30 m × 0.25 mm × 0.2 uml MSD: HP5793) were used to record the mass spectra. IR spectra were taken as KBr pellets on an ABB Bomem MB-100 FTIR spectrophotometer. IR is reported as characteristic bands (cm^{-1}) at their maximum intensity.

General Procedure for the One-Pot Reaction of Amines, CS_2, and α,β-Unsaturated Olefins

The support OH^-/silica was prepared according to a previously reported procedure[19] via using commercially available sodium hydroxide and silica gel starting materials (Table 2, entries 1–25).[17,18] The mixture was stirred at room temperature for 20 min, and then it was concentrated in vacuo and dried in a vacuum oven at 100 °C for 2 h. The mixture of amine (1 mmol), CS_2 (1 mmol), and OH^-/silica (0.1 g) was heated at 70 °C for 1 h. Then, methyl acrylate as the Michael acceptor (1 mmol) was added, and the entire mixture was stirred vigorously for 10 h. Finally, the solid mixture thus obtained was washed with ethyl acetate (10 mL), and OH^-/silica was filtered off. The organic solvent was removed under reduced pressure to give the desired product. The crude product was purified by recrystallization or column chromatography over silica gel to give the desired product. All products were characterized by melting point, IR, and NMR, and their physical data were similar to those reported in the literature.[17,18]

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