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A Facile and Efficient One-Pot Regioselective Synthesis of 2-Hydroxyalkyl Dithiocarbamates under Catalyst-Free Conditions

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ABSTRACT

A simple catalyst-free, and highly regioselective approach to 2-hydroxyalkyl dithiocarbamates is described which involves a one-pot reaction of various amines and carbon disulfide,CS_2, with epoxides in ethanol at room temperature.

Keywords: 2-Hydroxyalkyl Dithiocarbamates; Epoxides; Regioselective; Amines; Carbon Disulfide

1. Introduction

The formation of carbon-sulfur bond, especially under a green and safe condition, is an important transformation in organic synthesis. Sulfur containing compounds are found in many products of biological [1-4] and medical [5-7] relevance as well as in commercial drugs [8].

Dithiocarbamates are a class of fungicides extensively used worldwide on a range of crops mainly due to their efficiency in controlling plant fungal diseases and relatively low mammalian acute toxicity [9]. They have also received much attention due to their wide utility as potent anticancer agents [10,11] and cell apoptosis inhibitors [12-14]. Dithiocarbamates have found applications in the rubber industry as vulcanization accelerators [15], in controlled radical polymerization techniques [16-18], and recently in the synthesis of ionic liquids [19]. They also act as linkers in the solid-phase organic synthesis [20-22], and for protection of amine groups in peptide synthesis [23]. They are usually synthesized by several available methodologies [24-33].

In recent years, much attention has been paid to functionalized dithiocarbamates; among them, 2-hydroxy dithiocarbamates represent an important class of key compounds that have been used for various applications, especially as synthetic intermediates [34-36], as multifunctional lubricant additives [37,38], and as electrophotographic liquid developers [39,40]. They are usually synthesized by one of the following main methods: (1) reaction of an amine and carbon disulfide, to form dithiocarbamic acid salt, with epoxides [41,42], or with 2-hydroxyalkyl halides [43], and (2) reaction of amino-thiocarboxylic halides with 1,2-mercapto ethanol derivatives [44]. However, some of these procedures suffer from long reaction times, use of low temperatures, use of large excess of toxic carbon disulfide, use of strong basic conditions, and low to moderate yields of products. In two recent reports 2-hydroxy dithiocarbamates were directly prepared from primary or secondary amines, carbon disulfide and epoxides in acetone and in the presence of anhydrous potassium phosphate [41], and in catalyst- and solvent-free conditions [42]; in both methods, addition of an amine to CS_2 was slow, maintaining the temperature at around 0˚C followed by addition of an epoxide at room temperature.

2. Results and Discussion

One important issue in green chemistry which is currently receiving an increasing attention is the use of alternative reaction media that circumvent the problems associated with many of the traditional toxic and volatile organic solvents. Many issues surrounding a wide range of volatile and non-volatile, polar aprotic solvents have stimulated fine chemical and pharmaceutical industries to seek more benign alternatives [45]; there is a marked trend away from hydrocarbons and chlorinated hydrocarbons towards lower alcohols and ethers [45].

As part of our research to develop practical, simple, and green methodologies in organic synthesis [46-58], herein we describe an efficient, catalyst-free synthesis of 2-hydroxyalkyl dithiocarbamates from primary or secondary amines and CS_2 with epoxides in ethanol (**Scheme 1**).

In order to optimize the reaction condition with respect to solvent, time, temperature, and molar ratios of the

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components, the reaction of 2,3-epoxypropyl phenyl ether with benzylamine and carbon disulfide was planned as a model reaction in the absence of any catalyst. It was found that by simple initial mixing of benzylamine (1.2 mmol) and carbon disulfide (1.3 mmol) in ethanol (1.5 mL) at room temperature, followed by addition of the epoxide (1.0 mmol) at that temperature, the expected dithiocarbamates were obtained in 92% yield within a very short time. The reaction was also conducted in water but under the same reaction condition as above; however, it yielded no expected product even after 3.5 hrs.

To explore the generality and scope of this method, various amines (primary, secondary, benzylic and aromatic) and epoxides were examined under the conditions outlined above. As it can be seen from **Table 1**, the reaction of primary, secondary, and benzylic amines with epoxides are generally very fast (5 - 15 mins), clean and high yielding (60% - 98%), except for aniline (**Table 1**, Entry 9) which gave the corresponding dithiocarbamates but in poor yield (12%) even after 120 mins. In fact, as expected in a typical nucleophilic addition, aliphatic amines show higher reactivity than the aromatic ones. In all cases reported, only one single product was isolated. ^{1}H NMR Analysis of the pure dithiocarbamates obtained from their reaction with unsymmetrical epoxides revealed that in most cases the nucleophile predominantly attacks the less hindered carbon of the epoxide (C-a) (**Table 1**, Entries 1 - 6 and 10 - 14) to give mainly the regioisomer 3 (**Scheme 1**). However, under the same conditions, no selectivity was observed for styrene oxide, and both regioisomers 3 and 4 were formed (**Table 1**, Entries 15 - 18). As expected, in aliphatic epoxides steric factors predominate over electronic effects.

We assume that the unstable dithiocarbamic acid 5, initially generated from the amine and CS_2, reacts with the epoxide 2 giving rise to the formation of the 2-hydroxyalkyl dithiocarbamates 3 and 4 (**Scheme 2**).

3. Conclusion

To conclude, we have developed a very convenient and efficient regioselective and catalyst-free protocol for the one-pot reaction of various aliphatic/aromatic amines and CS_2 with different epoxides in ethanol at room temperature. In this fast and high yielding method, the use of low temperature is avoided.

4. Experimental

4.1. General

Melting points were recorded on a Buchi B-540 apparatus and were uncorrected. IR spectra were recorded on an ABB FTLA 2000 instrument. NMR spectra were recorded with either a Bruker AQS-300 or Bruker DRX-500 spectrometer with nominal frequencies of 300 MHz and 500 MHz for proton or 75 and 125 MHz for carbon, respecttively in $CDCl_3$ using TMS as an internal standard.

4.2. General Experimental Procedure for Preparation of 2-Hydroxyalkyl Dithiocarbamates

A stirred solution of carbon disulfide (1.3 mmol) in EtOH (1.5 ml) was slowly treated with the amine (1.2 mmol); the mixture was stirred for 15 mins at room temperature, followed by addition of the epoxides (1.0 mmol) in one portion; stirring, at room temperature, was continued for the length of time indicated in **Table 1**. After completion of the reaction, ethanol was evaporated, Et_2O (10 ml) was added, and the mixture was washed with water (2 × 5 ml), and the organic layer was dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the crude mixture was purified by preparative TLC (silica gel: eluent, *n*-hexane/EtOAc = 2:1).

Selected Physical and Spectral Data

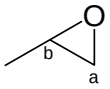
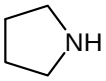
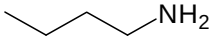
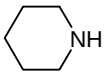
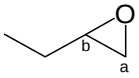
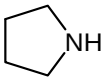
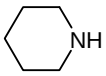
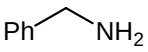
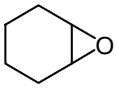
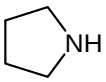
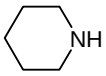
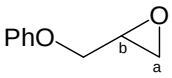
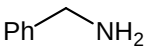
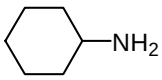
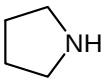
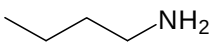
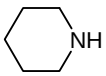
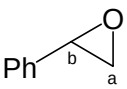
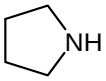
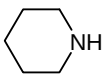
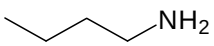
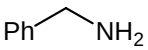
2-Hydroxypropyl *n*-Butyl Carbamodithioate (3b) [42] Colorless oil; IR (neat): ν_{max} = 750, 922, 1039, 1125, 1406, 3224, 3373 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H), 1.34 (sext, J = 7.1 Hz, 2H), 1.58 (quin, J = 7.6 Hz, 2H), 3.13 (dd, J = 14.7, 7.1 Hz, 1H), 3.34 (dd, J = 14.7, 3.2 Hz, 1H), 3.5 (br s, 1H), 3.63 (q, J = 6.9 Hz, 2H), 4.06 - 4.09 (br m, 1H), 8.44 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 20.1, 22.4, 30.2, 43.4, 47.3, 67.7, 197.2.

2-Hydroxybutyl Pyrrolidine-1-Carbodithioate (3d) [42] Colorless oil; IR (neat): ν_{max} = 750, 1219, 1432, 1463, 3404 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.4 Hz, 3H), 1.60 (quin, J = 7.3 Hz, 2H), 1.97 (quin, J = 6.9 Hz, 2H), 2.09 (quin, J = 6.9 Hz, 2H), 2.56 (br s, 1H), 3.38 (dd, J = 14.3, 7.4 Hz, 1H), 3.66 - 3.75 (m, 3H), 3.82 - 3.86 (m, 1H), 3.93 (t, J = 6.9 Hz, 2H).

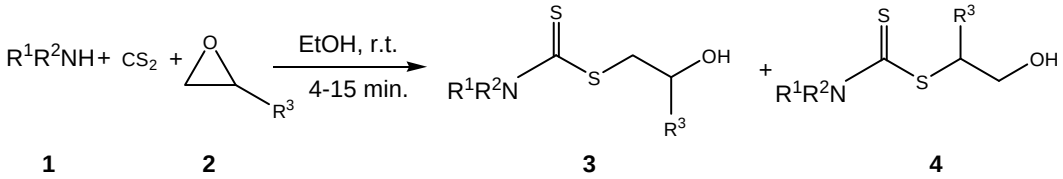
2-Hydroxybutyl Benzylcarbamodithioate (3f) [42] Yellow oil; IR (neat): ν_{max} = 703, 750, 938, 1094, 1234, 1391, 1499, 3209, 3337 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3H), 1.51 (quin, J = 7.4 Hz, 2H), 3.13 (dd, J = 14.7, 7.6 Hz, 1H), 3.36 (dd, J = 14.7, 3.1 Hz, 1H), 3.40 (br s, 1H), 3.72-3.77 (m, 1H), 4.84 (d, J = 5.3 Hz, 2H), 7.25-7.34 (m, 5H), 8.75 (br t, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.0, 29.3, 41.8, 51.1, 72.9, 127.9, 128.2, 128.8, 136.2, 198.1.

2-Hydroxy-3-Phenoxypropyl Piperidine-1-Carbamodithioate (3n) [42] Yellow oil; IR (KBr): ν_{max} = 1601, 2926, 3404 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64 (br s, 6H), 3.62 (dd, J = 14.3, 6.9 Hz, 2H), 3.80 (dd, J = 14.5, 3.8 Hz, 1H), 3.86 (br s, 2H), 4.05 (t, J = 4.8 Hz, 2H), 4.2-4.31 (m, 3H), 6.90 - 6.96 (m, 3H), 7.23-7.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2, 25.5, 26.0, 39.9, 51.6, 53.5, 69.6,70.5, 114.6, 121.1, 129.5, 158.5, 195.4.

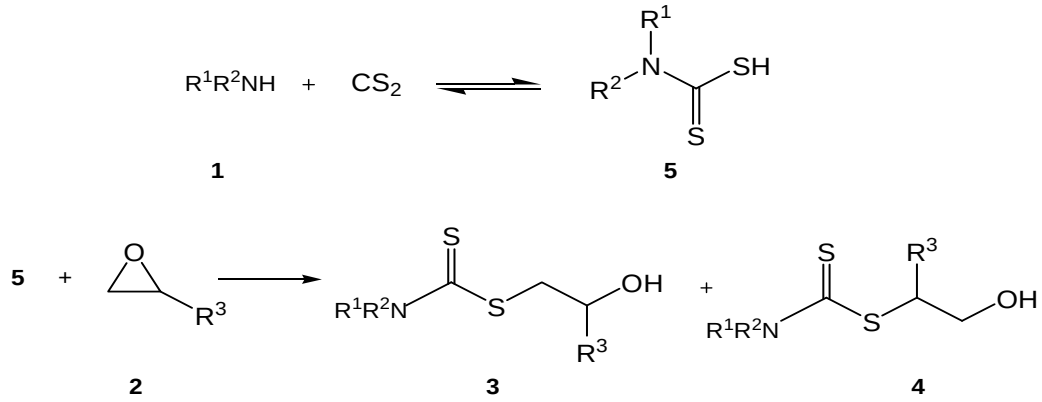
Table 1. Regioselective ring opening of epoxides in EtOH under catalyst-free conditions.

Entry	Epoxide	Amine	Reaction Time (min)	Product	Yield[a,b] (%)	Regioselectivity 3:4
1			8	3a	94	100:0
2			12	3b	91	82:18
3			8	3c	95	100: 0
4			6	3d	94	100:0
5			7	3e	94	100:0
6			12	3f	89	88:12
7			12	3g	60	-
8			13	3h	64	-
9		$PhNH_2$	120	3i	12	-
10			8	3j	92	100:0
11			7	3k	93	81:19
12			5	3l	98	100:0
13			10	3m	90	82:18
14			4	3n	96	100:0
15			10	3o/4o	90	35:65
16			10	3p/4p	91	57:43
17			15	3q/4q	83	33:67
18			12	3r/4r	88	62:38

[a]Isolated yield of 3 + 4; [b]Reference for known compounds [42].



Scheme 1. Preparation of 2-hydroxyalkyl dithiocarbamates.



Scheme 2. Proposed mechanism of formation of the dithiocarbamates.

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