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A FACILE GENERAL METHOD FOR THE PREPARATION OF S-METHYL THIOLCARBAMATES USING ZEOLITE CATALYSTS[#]

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Abstract: *Dimethyl carbonimidodithioates derived from various primary amines and amino acid esters (1) can be converted to S-methyl thiolcarbamates (2) by H-mordenite or H-Y zeolite catalysis in moderate to good yields.*

We have been engaged for the past several years in devising new synthetic reactions using zeolite catalysts, especially for industrial application. As part of this programme, we now report a simple, general method for the synthesis of S-alkyl thiolcarbamates from carbonimidodithioic acid esters.

There are very few general methods available for the preparation of S-alkyl thiolcarbamates. One of the earliest reported methods was the acid-catalyzed rearrangement of O-alkyl thionocarbamates to S-alkyl thiolcarbamates.[1] The acid catalyst used was p-toluenesulfonic acid or boron trifluoride-etherate.[2,3] Subsequently, the reaction of secondary amines with carbonyl sulfide, followed by S-alkylation has been shown to yield S-alkyl thiolcarbamates in good yields.[4] However, only secondary amines have been used in this reaction. Carbon monoxide acts as the source of the carbonyl group of S-alkyl thiolcarbamates in two recent processes. The first is the selenium-catalyzed reaction of amines with carbon monoxide and elemental sulfur, followed by alkylation.[5] Very recently, N,N-dialkylcarbamoyl lithium, generated from lithium dialkylamide and carbon monoxide, has been reacted with elemental sulfur and then alkylated to produce the desired S-alkyl thiolcarbamates.[6] Although the yields are good with secondary amines, the only primary amine tried, gave a complex mixture in this reaction.

The method we now report for the conversion of primary amines to N-substituted S-methyl thiolcarbamates has several advantages. The process uses a zeolite catalyst, which is easy to filter and recycle; it is therefore environmentally acceptable. The method avoids the use of carbon monoxide or carbonyl sulfide; the carbonyl group of the product is ultimately derived from carbon disulfide.

We had earlier reported[7] the condensation of N-methyl carbonimidodithioic acid dimethyl ester with nitromethane in presence of a zeolite to give 1-methylamino-1-methylthio-2-nitroethylene. During the scale-up of this process, we observed the formation of N-methyl S-methyl thiolcarbamate (2b) as a minor product (5-10%).

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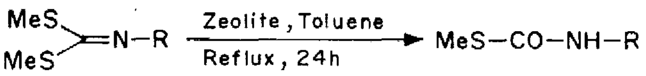
This prompted us to search for a suitable zeolite for the optimal conversion of **1** to **2**. Several zeolites were tried; among these H-mordenite and H-Y zeolites were found to be the most suitable for the conversion of **1** to **2**. This may be due to their large pore size and the presence of more active acidic sites present in these zeolite cavities (see Table 1). Presumably the imino nitrogen gets protonated inside the zeolite cavity; the resultant iminium system would be highly reactive towards nucleophilic attack by water present in the neighbourhood.

Table: 1 Composition of zeolite catalysts.[8]

zeolite	Si/Al ratio	pore size, nm
H-Y	2.43	0.74
H-Mordenite	10.06	0.70
H-ZSM-5	45.00	0.56
Na-Y	4.62	0.74



1

2

Scheme I

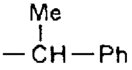
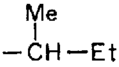
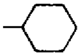
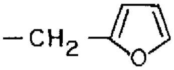
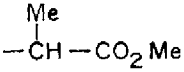
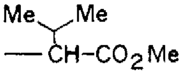
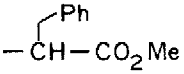
The starting dimethyl N-alkyl carbonimidodithioates (**1**) were prepared from alkylamines or amino acid esters and carbon disulfide by using reported methods.[9,10]

A typical procedure for the synthesis of S-methyl thiolcarbamate (**2**) is as follows: To a stirred solution of dimethyl N-(α-methylbenzyl) carbonimidodithioate (**1a**, 1 g derived from (S)-(-)-α-methylbenzylamine) in toluene (10 ml), H-mordenite (1 g) was added and the resulting mixture was refluxed for 24 h. It was then cooled and the zeolite was filtered off. The filtrate on concentration gave S-methyl N-(α-methylbenzyl) thiolcarbamate (**2a**)[11] (0.6 g, 70%) after purification by short column chromatography (silica gel, 3-5% ethyl acetate in hexane).

The generality of this reaction has been shown by using various dimethyl carbonimidodithioates (**1**) of different amines and amino acid esters to get corresponding S-methyl thiolcarbamates (**2**) in moderate to good yields.(see Table 2).

In conclusion we have developed a method for the synthesis of S-methyl thiolcarbamates using very mild reaction conditions.

Table: 2 Efficacy of zeolite catalysts in the conversion of **1** to **2**

compound[a]	R	m.p. (°C)	H-Mordenite[b]	HY[c]
2a	 $-\overset{\text{Me}}{\text{CH}}-\text{Ph}$	95.5 - 96.5	70	76
2b	$-\text{Me}$	liquid	37 (80)	35
2c	$-\text{Pr}^n$	liquid	42 (82)	36
2d	 $-\overset{\text{Me}}{\text{CH}}-\text{Et}$	semisolid	40 (78)	42
2e		103 - 104	72 (95)	70
2f	$-\text{CH}_2-\text{Ph}$	79 - 80	78 (95)	72
2g		semisolid	68 (90)	-
2h	$-\text{CH}_2-\text{CO}_2\text{Me}$	liquid	40 (50)	-
2i	$-\text{CH}_2-\text{CO}_2\text{CH}_2-\text{CH}_2-\text{Cl}$	73	43 (70)	-
2j	 $-\overset{\text{Me}}{\text{CH}}-\text{CO}_2\text{Me}$	46	50	-
2k	$-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{Me}$	semisolid	47 (75)	-
2l	 $-\overset{\text{CHMe}_2}{\text{CH}}-\text{CO}_2\text{Me}$	semisolid	45	-
2m	 $-\overset{\text{Ph}}{\text{CH}}-\text{CO}_2\text{Me}$	85 - 87	48	-

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a) All compounds gave satisfactory IR, ^{1}H NMR and Mass spectral data.

b) Isolated yields; figures in parenthesis indicate the yields based on starting material consumed.

c) Yields based on GC analysis.

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2. The yield has not been mentioned by the authors; in our hands, BF_3-Et_2O catalyzed rearrangement gave the product in 30-40% yield.

3. In our laboratory we have found that iodine or conc. sulfuric acid is the best catalyst for this transformation. (S.K. Tandel, S. Rajappa, unpublised observations).

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11. 2a: IR ($CHCl_3$): 3350, 1640, 1510, 1230 cm^{-1}; ^1H NMR ($CDCl_3$): 1.55 (d, 3H), 2.35 (s, 3H), 5.1 (m, 1H), 5.65 (br., 1H), 7.35 (m, 5H); MS (m/z): 195 (M^+).

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