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A General Synthesis of Isothiocyanates from Dithiocarbamates using Claycop

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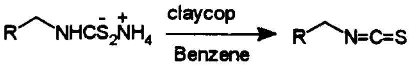
Abstract *: A Convenient and simple synthesis of alkyl, aryl and amino acid isothiocyanates is described by the decomposition of ammonium dithiocarbamates using Claycop in mild conditions.* © 1997 Elsevier Science Ltd.

Isothiocyanates are an importent class of compounds in organic chemistry[1]. They are used in the synthesis of heterocyclic derivatives[2] and some isothiocyanates have found applications in the synthesis of agrochemicals and pharmaceuticals[3]. Isothiocyanates have been mainly prepared by the reaction of amines with thiocarbonyl reagents like CS_2 and thiophosgene. However there are few methods for the preparation of isothiocyanates from thiourea and other chemicals. Among the literature methods, the most widely used procedure for the preparation of isothiocyanates is by the decomposition of dithiocarbamates[5]. There are few reagents[2b] like heavy metals, thiophosgene and iodine for this porpose. But some of these reagents are hazardous and toxic. Moreover, many of these recently developed methods require harsh reaction conditions and have limitations for their applictions.

Clay supported reagents[6,7] have recently found applications in organic synthesis because of their mild reacton conditions, easy availability and simple workup. In particular, the Claycop has been used for various conversions in organic synthesis[8]. In continuation of our work[9] using supported reagents in organic transformations, herein we wish to report the mild and simple procedure for the preparation of isothiocyanates by the decomposition of dithiocarbamates using Claycop. (scheme).

Scheme



In a typical procedure, the Claycop[10] (3 gm, 3 times by wt) was added to the suspension of freshly prepared ammonium dithiocarbamates[5] (0.01 mol) in benzene (30 ml). The mixture was stirred at r.t. and monitered by TLC (see table). After reaction was completed, the clay catalyst was removed by filteration. The product obtained by the removal of the solvent under vaccum and further purification was carried out by distillation or column chromatography.

The Claycop decomposes a variety of dithiocarbamates into corresponding isothiocyanates which supports the generality of this method. The mild condition and the safe reagent demonstrates the simplicity of this new method. The aryl dithiocarbamates are converted rapidly into isothioyanates whereas the alkyl dithiocarbamates reaction is slow (Table). We have observed that the reaction can also be accomplished in tolune without loss of the yield of isothiocyanate. The most important feature of this procedure is that it is also applicable for the preparation of amino acid acid isothiocyanates which are reported[11] to encounter with some difficulty or the use of thiophosgene.

In conclusion present method is mild, simple, convenient and applicable for the preparation of alkyl, aryl and amino acid isothiocyanates. Further this reaction should be useful for the preparation of peptide isothiocyanates.

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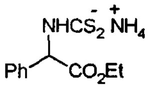
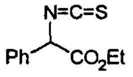
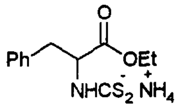
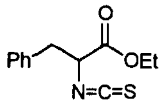
Table : Decomposition of Dithiocarbamates into Isothiocyanates using Claycop

Entry	R[a]	Products[b]	Time (h)	Yield[c]
1.	Phenyl	Phenyl isothiocyanate	1	85
2.	2-Methylphenyl	o-Methylphenyl isothiocyanate	1	77
3.	4-Chlorbenzyl	p-Chlorobenzyl isothiocyanate	1.5	75
4.	α-Methyl benzyl	α-Methyl Benzyl isothiocyanate	1	72
5.	1,2-Phenylene	Phenylene-1,2-diisothiocyanate	6	45
6.	Dodecyl[d]	Dodecyl isothiocyanate	5	52
7.			2.5	62
8.			3.	65

a) Ratio of dithiocarbamate to Claycop used 1:3 (by weight); b) All products were characterised by IR, ^{1}H NMR and Mass and by comparison with authentic samples; c) Yields of isolated products; d) In case of entry 6, the ratio of Claycop used is 1:6 by weight.

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