

SYNLETT Spotlight 462

Dithiocarbamates

Compiled by Veenu Bala



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Veenu Bala was born in Suratgarh, Rajasthan, India in 1984. She completed her BPharm degree in 2006 at Rajasthan University and received her MPharm degree in pharmaceutical chemistry from Uttar Pradesh Technical University (UPTU), Lucknow. Currently, she is working towards her Ph.D. in medicinal chemistry at AcSIR, Central Drug Research Institute (CSIR), Lucknow, under the guidance of Dr. Vishnu Lal Sharma. Her current research project involves design, synthesis, and biological evaluation of novel dithiocarbamates as dual-action spermicidal agents.

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Introduction

The dithiocarbamate functional group is an analogue of carbamate in which both oxygen atoms are replaced by sulfur atoms.

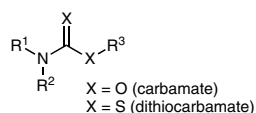


Figure 1

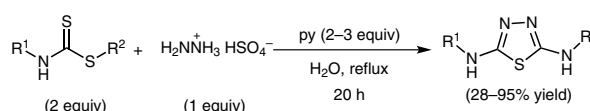
Organic dithiocarbamates have attracted attention because of their interesting chemistry and wide utility. They are valuable synthetic intermediates and their functional-

ization leads to the generation of derivatives which may possess diverse biological properties.

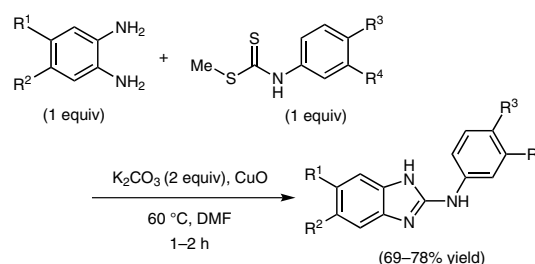
Dithiocarbamates are chain-transfer agents for RAFT polymerization,¹ and organic dithiocarbamates are used as substrates in radical chemistry² and as synthetic intermediates toward thioureas,³ amidines⁴ and guanidines.⁵ They are highly versatile mono-anionic chelating ligands which form stable complexes with transition elements possessing applications in medicine.⁶ Various dithiocarbamate salts can be easily prepared in high yields from amines, and they are soluble in water or organic solvents. Primary and secondary amines easily react with carbon disulfide and sodium hydroxide to form dithiocarbamate salts.

Abstracts

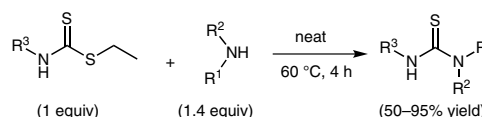
(A) Halimehjani et al. utilized dithiocarbamates as efficient intermediates for the synthesis of symmetrical substituted 2,5-diamino-1,3,4-thiadiazoles in water. Reaction of the easily prepared dithiocarbamates with hydrazinium salt gave the corresponding thiadiazoles in moderate to good yields.⁷



(B) Das et al. described an efficient and practical procedure for the synthesis of a wide variety of 2-(*N*-substituted)aminobenzimidazoles using dithiocarbamates and a catalytic amount of CuO. This procedure can be used to synthesize potential drug candidates with antiallergic and antihistamine properties.⁴



(C) An efficient method for the synthesis of unsymmetrical thioureas from readily synthesized *S*-alkyl dithiocarbamates and amines without using any catalyst under solvent-free conditions was developed. The short reaction time, high yield, simple work-up, and solvent-free conditions are advantages of this method.⁸



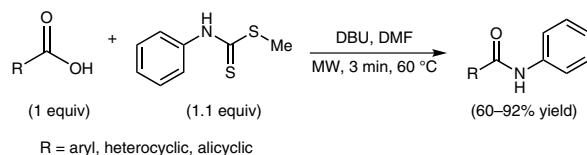
SYNLETT 2014, 25, 0746–0747

Advanced online publication: 23.01.2014

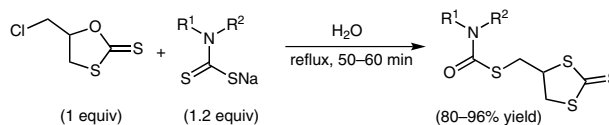
DOI: 10.1055/s-0033-1340637; Art ID: ST-2013-V0469-V

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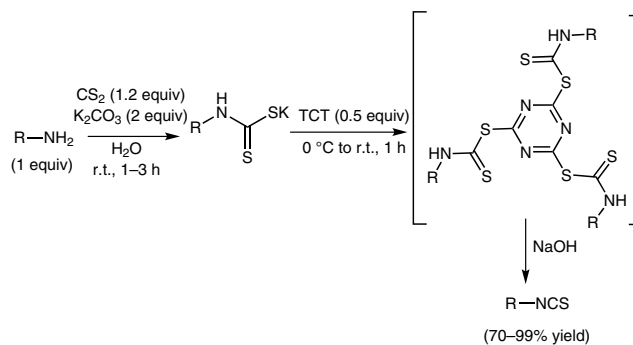
(D) Katari et al. have reported an efficient one-pot amide-bond formation under microwave conditions employing substituted acids and dithiocarbamates as the amine source. Various bases (including pyridine, DABCO, and DMAP) were screened, and DBU in DMF gave the best yield.⁹



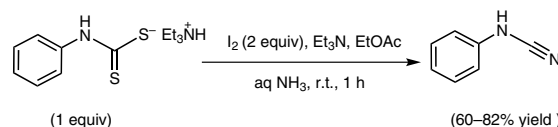
(E) Lal et al. reported a facile synthesis of *S*-(2-thioxo-1,3-dithiolan-4-yl)methyl dialkylcarbamothioates by the reaction of 5-(chloromethyl)-1,3-oxathiolane-2-thione with sodium dialkylcarbamodithioates through intermolecular O–S rearrangement in water. The authors tried different solvents, and a significant rate enhancement was observed in water compared to organic solvents.¹⁰



(F) Sun et al. developed a general and facile one-pot process for the synthesis of isothiocyanates from amines under aqueous conditions. This method is advantageous for the synthesis of highly electron deficient aromatic isothiocyanates. It involves an in situ generation of a dithiocarbamate salt to form the isothiocyanate product, with trichlorotriazine (TCT) as the desulfurylation reagent.¹¹



(G) Nath et al. developed an efficient one-pot procedure for the synthesis of cyanamides from their corresponding dithiocarbamic acid salts via a double desulfurization strategy using molecular iodine. It involves in situ generation of the isothiocyanate followed by conversion into thiourea which undergoes oxidative desulfurization to yield cyanamide. Environmental benignity, cost effectiveness, and high yields are important attributes of this procedure.¹²



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