SYNLETT Spotlight 323

Bis(benzotriazolyl)methanethione

Compiled by Archana Singh

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

Archana Singh was born in Varanasi, Uttar Pradesh, India, in 1981. She obtained her B.Sc. from the P. G. College in 2003 and her M.Sc. in chemistry from the U. P. College, Varanasi, in 2005. She joined the research group of Dr. Vinod K. Tiwari at the Banaras Hindu University. Her current research is focused on the development of new synthetic methodologies and on carbohydrate synthesis for medicinal interests.

Senior Research Fellow, Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
E-mail: archana_chembhu@yahoo.co.in

Introduction

Bis(benzotriazolyl)methanethione, a reagent derived from benzotriazole, is a thiophosgene equivalent for thioacylations and for the synthesis of different thiocarbonyl compounds.^{1,2} Compared to thiophosgene, bis(benzotriazolyl)methanethione is found to be more advantageous due to its high stability and less toxicity. It is a crystalline solid, easy to handle, and it can be stored for years at room temperature. Bis(benzotriazolyl)methan-

ethione can be obtained in high yield as yellow crystals (mp 170–171 °C) starting from benzotriazole (Scheme 1).³

Scheme 1

Abstracts

(A) Katritzky et al. used 1-(alkyl/arylthiocarbomoyl)benzotriazoles as isothiocyanate equivalents for the efficient synthesis of secondary and tertiary thioureas in high yield.⁴

(B) A facile protocol for the synthesis of diverse 2-thioxo-2,3-dihydroquinazolin-4(1H)-ones by one-pot reaction of anthranilic acid esters, primary amines, and bis(benzotriazolyl)methanethione in the presence of the amidine base DBU has been reported previously.^{5a,b}

(C) Further, a one-pot methodology for diverse dithiocabamates including N/S glycosyl dithiocabamates with various substituents at the thiol, at the amine or at both chains by the reaction of mercaptans, amines, and bis(benzotriazolyl)methanethione in the presence of DBU has been developed.^{6a,b}

(D) (Bisbenzotriazol-1-yl-methylene)amines, benzotriazole-1-carboxamidines, and benzotriazole-1-carboximidamides can be synthesized using bis(benzotriazole-1-yl)methanethione reagents. They can readily react with diverse hydroxylamine and hydrazine giving mono-, symmetrical di-*N*-hydroxy- and *N*-aminoguanidines with different substitution patterns in good yields.⁷

(E) Thiosemicarbazides and *N*-hydroxythioureas of diverse substitution patterns have also been synthesized using bis(benzotriazole-1-yl)methanethione as a precursor by reaction of the appropriate hydrazine and corresponding hydroxylamine, respectively.⁸

(F) The Diels–Alder addition of bis(benzotriazole-1-yl)methanethione to cyclopentadiene provides the moisture-stable crystalline adduct.⁹

(G) Katritzki et al. have reported the synthesis of acyclic and cyclic 1,2,3-trisubstituted guanidines¹⁰ in high yield with a convenient method for the guanylation of various primary and secondary amines by the use of (bisbenzotriazol-1-yl-methylene)amines and benzotriazole-1-carboxamidines. These reagents are prepared by bis(benzotriazole-1-yl)methanethione.

(H) Sasmal et al. reported a bis(benzotriazole-1-yl)methanethione-mediated one-pot methodology for the synthesis of the thiazol ring via *N*-desilylation and thioacylation followed by cycloisomerization in an intramolecular thia-Michael fashion.¹¹

References

- (1) (a) Katritzky, A. R.; Belyakov, S. A. *Aldrichimica Acta* **1998**, 31, 35. (b) Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, 98, 409.
- (2) Katritzky, A. R.; Witek, R. M.; Rodriguez-Garcia, V.; Mohapatra, P. P.; Rogers, J. W.; Cusido, J.; Abdel-Fattah, A. A. A.; Steel, P. J. *J. Org. Chem.* **2005**, 70, 7866.
- (3) Orth, R. E.; Soedigdo, S. *J. Heterocycl. Chem.* **1965**, 2, 486.
- (4) Katritzky, A. R.; Ledoux, S.; Witek, R. M.; Nair, S. K. *J. Org. Chem.* **2004**, 69, 2976.
- (5) (a) Tiwari, V. K.; Singh, D. D.; Hussain, H. A.; Mishra, B. B.; Singh, A. *Monatsh. Chem.* **2008**, 139, 43. (b) Tiwari, V. K.; Kale, R. R.; Mishra, B. B.; Singh, A. *ARKIVOC* **2008**, (xiv), 27.
- (6) (a) Tiwari, V. K.; Singh, A.; Hussain, H. A.; Mishra, B. B.; Tripathi, V. J. *Monatsh. Chem.* **2007**, 138, 653. (b) Singh, A.; Kate, R. R.; Tiwari, V. K. *Trends in Carbohydrate Research* **2009**, 1, 80.
- (7) Katritzky, A. R.; Khashab, N. M.; Bobrov, S.; Yoshioka, M. *J. Org. Chem.* **2006**, 71, 6753.
- (8) Katritzky, A. R.; Khashab, N. M.; Gromova, A. V. *ARKIVOC* **2006**, (iii), 226.
- (9) Larsen, C.; Harpp, D. N. *J. Org. Chem.* **1980**, 45, 3713.
- (10) Katritzky, A. R.; Khashab, N. M.; Bobrov, S. *Helv. Chim. Acta* **2005**, 88, 1664.
- (11) Sasmal, P. K.; Sridhar, S.; Iqbal, J. *Tetrahedron Lett.* **2006**, 47, 8661.