SYNLETT Spotlight 139

Sodium Methylsulfinylmethylide: A Versatile Reagent

Compiled by Mukulesh Mondal

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

Mukulesh Mondal completed his B.Sc. at Suri Vidyasagar College, Burdwan University and his M.Sc. at Burdwan University, West Bengal, India. He received a research fellowship after qualifying the UGC-National Eligibility Test (NET) and joined the research group of Dr. N. P. Argade at National Chemical Laboratory, Pune, India. His Ph.D. work focuses on the total synthesis of bioactive natural products and the development of new synthetic methodologies for the synthesis of bioactive natural and unnatural benzofurans and benzopyrans.

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, Maharashtra, India
Fax +91(20)25893153; E-mail: mukuleshm@yahoo.com

Introduction

Sodium methylsulfinylmethylide (sodium dimsylate, dimsylsodium), introduced by Corey and Chaykovsky,¹ has found widespread use² in organic synthesis because of its strong basic character, nucleophilicity and its use for the introduction of methylsulfinylmethyl group. It is conveniently prepared¹ by heating finely powdered sodium hydride in an excess of anhydrous DMSO under nitrogen at about 70 °C until hydrogen evolution stops, resulting in a clear solution. Sodium amide can also be used as the base.³

The reagent is highly soluble in DMSO and such solutions are sensitive to heat and air, and decompose rapidly above 85 °C.⁴ At 20 °C they lose 8% of their activity per week. Hence, it is probably best prepared when needed and used immediately. However, an ultrasound-mediated preparation⁴ has been reported for long-time storage of the reagent. Purity can be checked by titration with form-anilide using triphenylmethane as an indicator (colorless to deep red).¹

Abstracts

(A) Strained cyclopropanes substituted with multi-nitro groups are of interest as high-energy materials. They have been prepared by oxidative cyclization of sodium methylsulfinylmethylide generated 1,3-dinitronate dianions with iodine in DMSO.⁵

(B) Optically active 3-butene-1,2-diol has also been prepared in a stereoselective manner by epoxide ring opening with sodium methylsulfinylmethylide at the TMS-substituted carbon followed by desilylation and sulfenate elimination.⁶

(C) Sodium methylsulfinylmethylide mediated one-pot dehydrobromination and deacylation of vinylic bromoesters are known to furnish alkynyl alcohols in good yield.⁷

(D) Sodium methylsulfinylmethylide generated bis-ylide undergoes an oxidative coupling in the presence of molecular oxygen to form a cyclic alkene.⁸

(E) Sodium methylsulfinylmethylide reacts with ketone in DMSO to produce γ -unsaturated thiols via [2,3]-sigmatropic rearrangement of β -unsaturated sulfinyl carbanions.⁹

(F) Combination of dimethylsulfonium methylide and sodium methylsulfinylmethylide acts as an equivalent of carbene and undergoes addition with 2-arylmethylidene-2-phosphonoacetate, and its subsequent reaction with an aldehyde is known to furnish 1,2,3-trisubstituted-1,3-butadienes.¹⁰

(G) Wittig reaction of the 5-methylfurfural with the ylide generated in situ from the reaction of (8-hydroxyoctyl)triphenylphosphonium bromide and sodium methylsulfinylmethylide furnishes a mixture of *Z* and *E* olefins in high yield.¹¹

(H) *N*-Arylmethylberbinium, on treatment with sodium methylsulfinylmethylide in DMSO, undergoes Stevens rearrangement to produce 8-(arylmethyl)berbine in high yield.¹²

(I) Carboxylate-stabilized sulfur ylide generated in the presence of sodium methylsulfinylmethylide reacts directly with aldehydes and ketones to give epoxides in DMSO or THF–DMSO mixtures.¹³

References

- (1) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345.
- (2) (a) Durst, T. *Adv. Org. Chem.* **1969**, *6*, 285. (b) Hauthal, H. G.; Lorenz, D. In *Dimethyl Sulfoxide*; Martin, D.; Hauthal, H. G., Eds.; Wiley: New York, **1971**, 349–374.
- (3) Kaiser, E. M.; Braed, R. D.; Hauser, C. R. *J. Organomet. Chem.* **1973**, *59*, 53.
- (4) Sjöberg, S. *Tetrahedron Lett.* **1966**, 6383.
- (5) Wade, P. A.; Dailey, W. P.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 5452.
- (6) (a) Takano, S.; Tomita, S.; Iwabuchi, Y.; Ogasawara, R. *Synthesis* **1988**, 610. (b) Kobayashi, Y.; Ito, Y. I.; Urabe, H.; Sato, F. *Synlett* **1991**, 813.
- (7) Grattan, T. J.; Whitehurst, J. S. *J. Chem. Soc., Perkin Trans. I* **1990**, 11.
- (8) (a) Romo, D.; Meyers, A. I. *J. Org. Chem.* **1992**, *57*, 6265. (b) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5298. (c) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5321. (d) Gonsey, I.; Rowley, A. G. In *Organophosphorous Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: London, **1979**, 17–153. (e) Deyrup, J. A.; Betkouski, M. F. *J. Org. Chem.* **1975**, *40*, 284.
- (9) Fokin, A. A.; Kushko, A. O.; Kirij, A. V.; Yurchenko, A. G.; Schleyer, P. R. *J. Org. Chem.* **2000**, *65*, 2984.
- (10) Date, S. M.; Ghosh, S. K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2099.
- (11) Mondal, M.; Argade, N. P. *Tetrahedron Lett.* **2004**, *45*, 5693.
- (12) Valpuesta, M.; Diaz, A.; Suau, R.; Torres, G. *Eur. J. Org. Chem.* **2004**, 4313.
- (13) Aggarwal, V. K.; Hebach, C. *Org. Biomol. Chem.* **2005**, *3*, 1419.