

SYNLETT Spotlight 139

Sodium Methylsulfinylmethylide: A Versatile Reagent

Compiled by Mukulesh Mondal



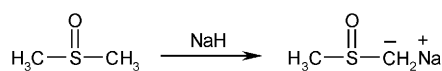
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

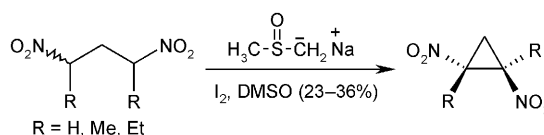
Sodium methylsulfinylmethylide (sodium dimsylate, dimsylsodium), introduced by Corey and Chaykovsky,¹ has found widespread use² in organic synthesis because of its strong basic character, nucleophilicity and its use for the introduction of methylsulfinylmethyl group. It is conveniently prepared¹ by heating 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



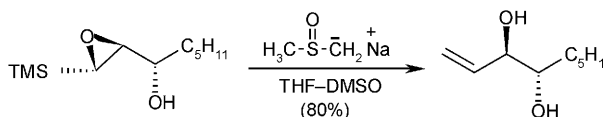
The reagent is highly soluble in DMSO and such solutions are sensitive to heat and air, and decompose rapidly above 85 °C.⁴ At 20 °C they lose 8% of their activity per week. Hence, it is probably best prepared when needed and used immediately. However, an ultrasound-mediated preparation⁴ has been reported 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

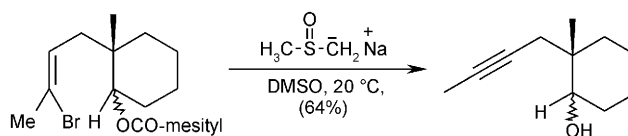
(A) Strained cyclopropanes substituted with multi-nitro groups are of interest as high-energy materials. They have been prepared by oxidative cyclization of sodium methylsulfinylmethylide generated 1,3-dinitronate dianions with iodine in DMSO.⁵



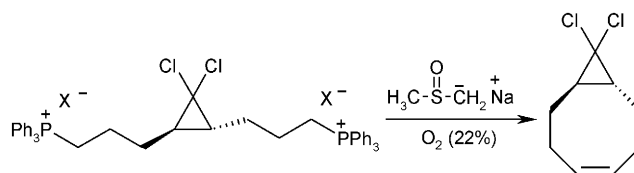
(B) Optically active 3-butene-1,2-diol has also been prepared in a stereoselective manner by epoxide ring opening with sodium methylsulfinylmethylide at the TMS-substituted carbon followed by desilylation and sulfenate elimination.⁶



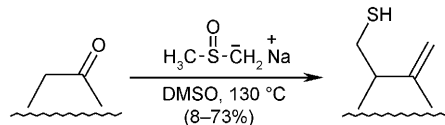
(C) Sodium methylsulfinylmethylide mediated one-pot dehydrobromination and deacylation of vinylic bromoesters are known to furnish alkynyl alcohols in good yield.⁷



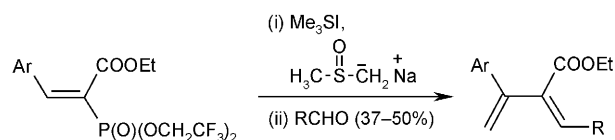
(D) Sodium methylsulfinylmethylide generated bis-ylide undergoes an oxidative coupling in the presence of molecular oxygen to form a cyclic alkene.⁸



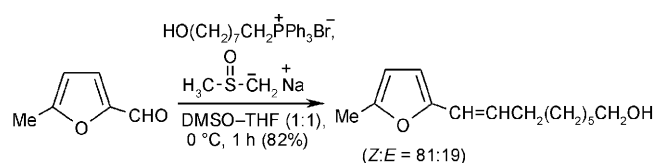
(E) Sodium methylsulfinylmethylide reacts with ketone in DMSO to produce γ -unsaturated thiols via [2,3]-sigmatropic rearrangement of β -unsaturated sulfinyl carbanions.⁹



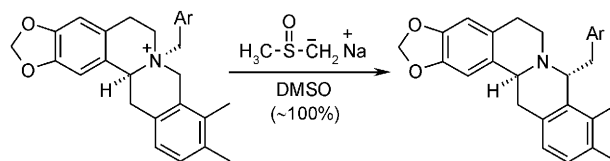
(F) Combination of dimethylsulfonium methylide and sodium methylsulfinylmethylide acts as an equivalent of carbene and undergoes addition with 2-arylmethylidene-2-phosphonoacetate, and its subsequent reaction with an aldehyde is known to furnish 1,2,3-trisubstituted-1,3-butadienes.¹⁰



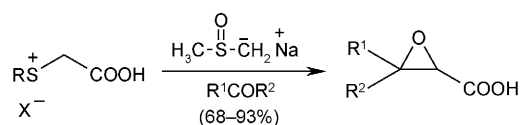
(G) Wittig reaction of the 5-methylfurfural with the ylide generated in situ from the reaction of (8-hydroxyoctyl)triphenylphosphonium bromide and sodium methylsulfinylmethylide furnishes a mixture of *Z* and *E* olefins in high yield.¹¹



(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

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