

# SYNLETT Spotlight 240

## Dimethylsulfoxonium Methylide (DSM): A Versatile Reagent

Compiled by Chhama Awasthi



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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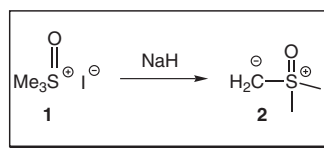
Dedicated to my honorable mentor Prof. L. D. S. Yadav

### Introduction

Dimethylsulfoxonium methylide (DSM), also known as Corey–Chaykovsky reagent, has proved to be a versatile nucleophilic reagent capable of reacting with different chemical systems. Its industrial availability coupled with its potential to achieve original chemical transformations makes it a reagent of choice for the synthesis of new leads and innovative substances. It has found wide application in organic synthesis such as epoxidation,<sup>1</sup> cyclopropanation,<sup>2,3</sup> aziridination,<sup>4</sup> extension of esters,<sup>5</sup> diolefination of cycloalkanones,<sup>6</sup> ring transformation,<sup>7</sup> polymerization,<sup>8</sup> formation of silyl enol ethers,<sup>9</sup> ring opening,<sup>10,11</sup> and formation of chiral spiro[2.5]octanones by methylenation of cyclohexanones.<sup>12</sup>

### Preparation

In 1962, Corey and Chaykovsky performed the synthesis of dimethylsulfoxonium methylide **2** by proton transfer of readily accessible trimethylsulfoxonium halides **1** to a strong base. Solutions of **2** in dimethyl sulfoxide were prepared from the iodide (or chloride) **1** by stirring with one equivalent of powdered sodium hydride under nitrogen at room temperature (rapid evolution of hydrogen, exothermic).<sup>13</sup>

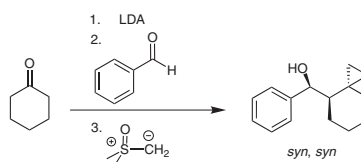


Scheme 1

### Abstract

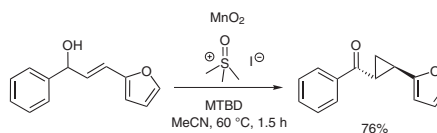
#### (A) Epoxidation:

Recently, Hansen and co-workers have reported a DSM-promoted tandem aldol–epoxidation reaction which constructs three new stereocenters with complete diastereoselectivity.<sup>1</sup>



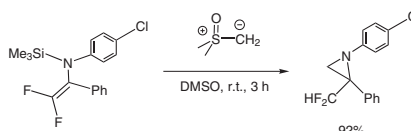
#### (B) Cyclopropanation:

One-pot oxidative cyclopropanation reactions of activated alcohols can be brought about by DSM.<sup>2</sup>



#### (C) Aziridination:

Dimethylsulfoxonium methylide affords difluoromethylaziridines upon reaction with difluoro enamines.<sup>4</sup>



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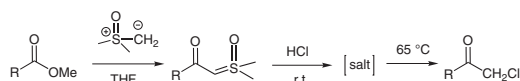
Advanced online publication: 07.05.2008

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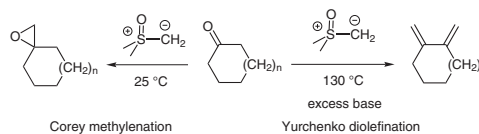
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**(D) Extension of Esters:**

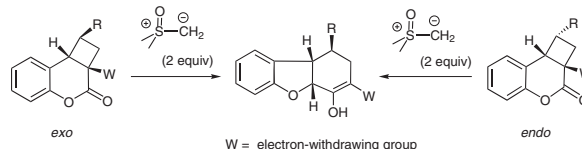
Using dimethylsulfoxonium methylide, a variety of methyl esters can be converted into  $\alpha$ -chloro ketones with extension of the carbon chain.<sup>5</sup>

**(E) Diolation of Cycloalkanones:**

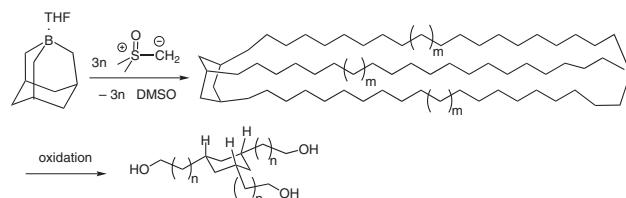
Terminal/exocyclic 1,3-dienes are widely used in synthetic organic chemistry. Very recently, Butova and co-workers have synthesized exocyclic 1,3-dienes by a one-pot diolation of cyclic ketones employing DSM and excess of a base at 130 °C. Under these conditions the Corey reaction is suppressed and terminal 1,3-dienes are formed instead of epoxides. This reaction is termed as Yurchenko diolation.<sup>6</sup>

**(F) Ring Transformation:**

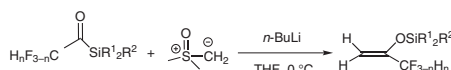
Coumarin derivatives with electron-withdrawing group at position 3 have been reported to undergo a novel ring transformation with DSM, which has been applied to the second-generation synthesis of ( $\pm$ )-linderol A.<sup>7</sup>

**(G) Polymerization:**

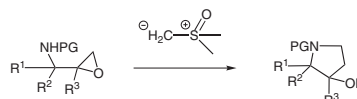
Trialkyl and triaryl organoboranes undergo multiple, repetitive homologation upon reaction with DSM. The polyhomologation of 1-boraadamantane·THF with DSM generates a novel macrocyclic trialkylborane, which upon oxidation affords three-armed star polymethylene polymer incorporating a *cis,cis*-1,3,5-trisubstituted cyclohexane core.<sup>8</sup>

**(H) Formation of Silyl Enol Ethers:**

Dimethylsulfoxonium methylide has been demonstrated to react with mono- and difluoroacetyltrialkylsilanes to give enol silyl ether products exclusively.<sup>9</sup>

**(I) Ring Opening:**

*N*-Tosyl-protected 3-hydroxypyrrolidines are prepared by reaction of DSM with readily available epoxysulfonamides via regioselective ring-opening followed by 5-*exo-tet* cyclization in preference to oxetane formation.<sup>10</sup>

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