

# SYNLETT Spotlight 357

## Samarium Triiodide

Compiled by Yuanmin Zhang

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

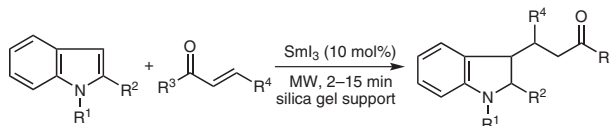
### Introduction

Samarium triiodide ( $\text{SmI}_3$ ) is a yellow powder with a melting point of  $820^\circ\text{C}$ , unstable towards air and moisture. It is commercially available and has been widely used in organic reactions, such as elimination, conjugate

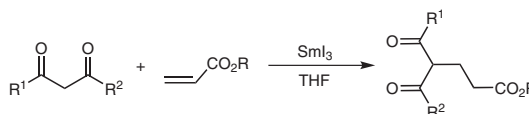
addition, carbonyl reduction, intramolecular cyclization and nucleophilic substitution reactions. It can also be regarded as an efficient metal catalyst and a Lewis acid catalyst to accelerate reactions and to improve yields for organic transformations. Herein, the applications of  $\text{SmI}_3$  in recent years are listed and reviewed.

### Abstracts

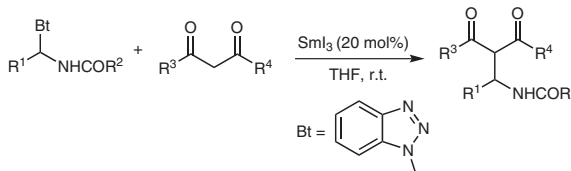
(A) A novel and highly efficient method for the conjugate addition of indoles with electron-deficient olefins catalyzed by  $\text{SmI}_3$  afforded a series of new 3-substituted indole derivatives.<sup>1,2</sup> This reaction is highly regioselective and can be accelerated by microwave irradiation with silica gel as catalyst support.<sup>3</sup>



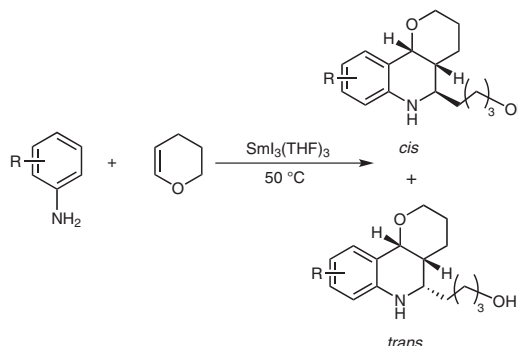
(B) The Michael reaction of  $\beta$ -diketones with  $\alpha,\beta$ -unsaturated esters catalyzed by samarium triiodide was achieved in THF under reflux to give the corresponding  $\delta$ -carbonyl esters in good yields.<sup>4</sup>



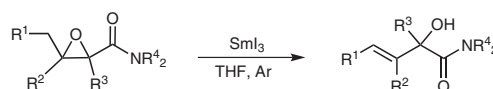
(C) The nucleophilic substitution reaction between *N*-(1-benzotriazol-1-ylalkyl)amides and 1,3-dicarbonyl compounds promoted by samarium triiodide was reported. This provides a useful method for the preparation of Mannich-type products with good yields and high diastereoselectivities.<sup>5</sup>



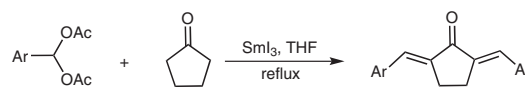
(D) Catalyzed by  $\text{SmI}_3$ , a series of arylamines reacted with dihydropyran to give pyrano[3,2-*c*]quinoline derivatives in moderate to good yields with high *trans* diastereoselectivity.<sup>6</sup>



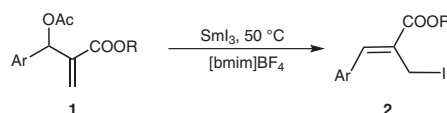
(E) A simple methodology to prepare (*E*)- $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated amides from  $\alpha,\beta$ -epoxyamides, by using catalytic samarium triiodide, has been developed. This elimination reaction proceeds with total or high diastereoselectivity and regioselectivity.<sup>7</sup>



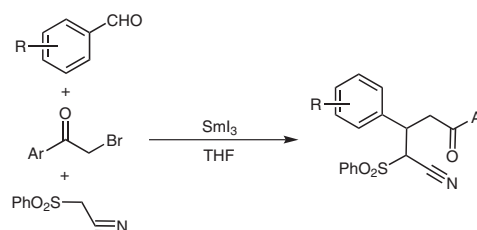
(F) 1,1-Diacetates undergo deprotection and condensation reaction with cycloalkanones in the presence of catalytic samarium triiodide to afford  $\alpha,\alpha'$ -bis(substituted benzylidene)cycloalkanones in good yields.<sup>8</sup>



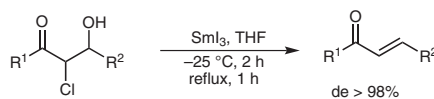
(G) A new and facile method to prepare (*Z*)-allylic iodides **2** from the acetates of Baylis–Hillman adducts **1** mediated by samarium triiodide was developed in ionic liquid [bmim]BF<sub>4</sub> with excellent yields and good stereoselectivity.<sup>9</sup>



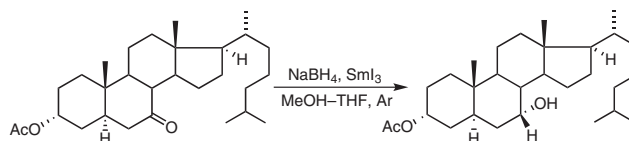
(H) A novel, one-pot three-component reaction of aldehydes,  $\alpha$ -halo ketones and (phenylsulfonyl)acetonitrile was achieved in good yields in the presence of samarium triiodide.<sup>10</sup>



(I) SmI<sub>3</sub>-promoted  $\beta$ -elimination reactions of  $\alpha$ -chloro- $\beta$ -hydroxy ketones offer a highly efficient way to synthesize  $\alpha,\beta$ -unsaturated ketones in good yields and *E*-diastereoselectivity.<sup>11</sup>



(J) Samarium triiodide can also be used for the catalytic reduction of the saturated steroidal ketone into the corresponding secondary alcohol.<sup>12</sup>



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