

# SYNLETT Spotlight 442

## Diiodomethane: A Versatile C1 Building Block

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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

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### Introduction

Diiodomethane, better known as methylene iodide, is a dense (3.325 g/mL at 25°C), light-sensitive, pale-yellow liquid. Because of its high density, it is used by the gemological industry to determine the density of minerals.<sup>1</sup> Being such an interesting compound, diiodomethane is a versatile C<sub>1</sub> building block, which can be used to form carbon–carbon and carbon–heteroatom bonds. It is an easy-to-handle compound and can be used in a wide number of different reactions such as epoxidation,<sup>2</sup> diazotization,<sup>3</sup>

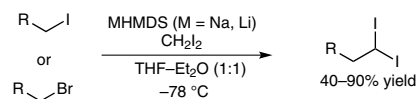
iodomethylation,<sup>4</sup> cyclopropanation,<sup>5</sup> alkene reduction,<sup>6</sup> and sigmatropic rearrangement.<sup>7</sup> In the presence of metallic samarium, the air-sensitive samarium diiodide (SmI<sub>2</sub>) is formed in situ; this is cheaper than buying samarium diiodide.<sup>8</sup>

Diiodomethane is commercially available, but can also be prepared by mixing methylene dichloride and sodium iodide in dimethylformamide at a constant temperature of 100 °C for 6–8 hours.<sup>9</sup>

### Abstracts

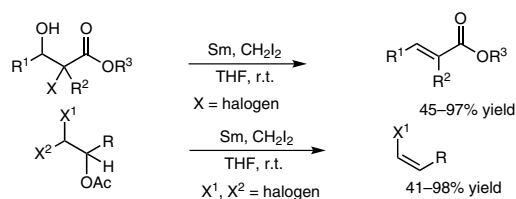
#### (A) Alkylation of Diiodomethane

Bull and Charette reported an improved procedure to obtain functionalized *gem*-diiodoalkanes with acceptable functional group tolerance towards olefins, acetals, ethers, carbamates, and hindered esters.<sup>10</sup>



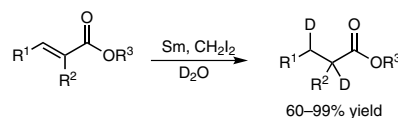
#### (B) $\beta$ -Elimination of 2-Halogen-3-hydroxyesters and Synthesis of (Z)-Vinyl Halides

(*E*)- $\alpha,\beta$ -Unsaturated esters were synthesized from 2-halo-3-hydroxyesters in good to excellent yields using a mixture of metallic samarium and diiodomethane. (*Z*)-Vinyl halides can be obtained with high diastereoselectivities and yields from O-acetylated 1,1-diiodo alcohols, metallic samarium, and diiodomethane in THF at room temperature.<sup>8</sup>



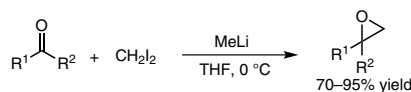
#### (C) Synthesis of 2,3-Dideuterioesters

The 1,4-reduction of  $\alpha,\beta$ -unsaturated esters with D<sub>2</sub>O in the presence of metallic samarium and diiodomethane afforded the corresponding 2,3-dideuterioesters in good to excellent yields.<sup>6</sup>



#### (D) Transformation of Carbonyl Compounds into Epoxides

Epoxides are important because they can be opened by a variety of nucleophiles to afford 1,2-difunctionalized systems. Concellón et al. reported a general, easy, and simple transformation of aldehydes and ketones into epoxides with excellent yields using diiodomethane and methylolithium at 0 °C.<sup>2</sup>



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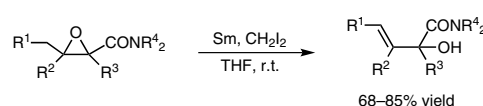
Advanced online publication: 17.07.2013

DOI: 10.1055/s-0033-1338964; Art ID: ST-2013-V0449-V

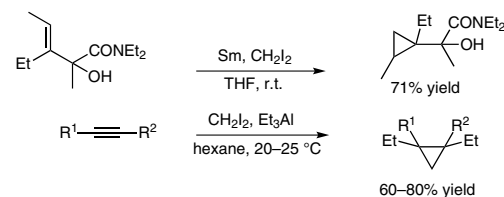
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(E) *Synthesis of (E)- $\alpha$ -Hydroxy- $\beta,\gamma$ -unsaturated Amides*

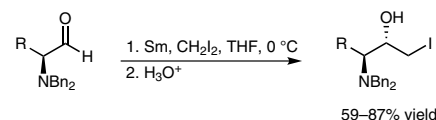
Concellón and co-workers<sup>11</sup> reported an easy and simple procedure to prepare (E)- $\alpha$ -hydroxy- $\beta,\gamma$ -unsaturated amides using metallic samarium and diiodomethane with high regio- and diastereoselectivity.

(F) *Cyclopropanation*

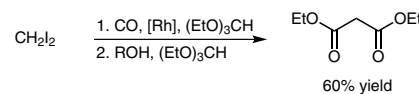
Cyclopropanation of alkenes can be carried out by a mixture of metallic samarium and diiodomethane.<sup>11</sup> Cyclopropanation of terminal alkynes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.<sup>5</sup>

(G) *Iodomethylation of Amino Aldehydes*

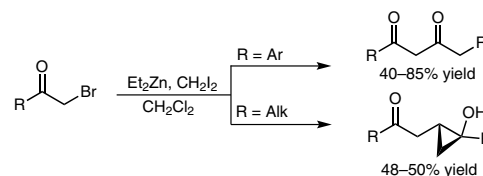
The halomethylation of carbonyl compounds is difficult to achieve due to the instability of halomethyl lithium compounds. As an alternative, Bernad et al. reported a smoothly proceeding reaction using metallic samarium and diiodomethane.<sup>4</sup>

(H) *Double Carbonylation of Diiodomethane*

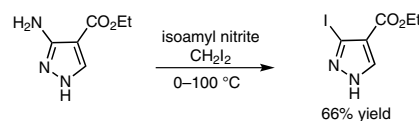
Double carbonylation of diiodomethane in triethylorthoformate in the presence of catalytic amounts of rhodium complex gave diethylmalonate in good yield.<sup>12</sup>

(I) *Sigmatropic Rearrangement*

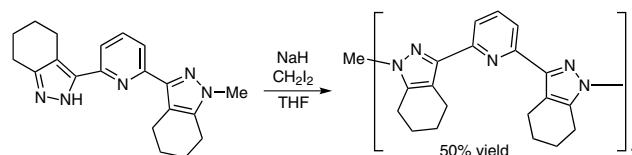
Li and co-workers described an efficient method for the synthesis of  $\beta$ -diketones from aromatic  $\alpha$ -bromo ketones in the presence of diiodomethane and diethylzinc. Aliphatic  $\alpha$ -bromomethyl ketones gave 2,4-disubstituted furans or cyclopropanols in moderate yield.<sup>7</sup>

(J) *Diazotization for the Synthesis of Aryl Iodides*

The reactions of aryl amines in the presence of isoamyl nitrite and diiodomethane formed aryl iodides cleanly and in good yield.<sup>3</sup>

(K) *Coupling Molecules with a CH<sub>2</sub> Linkage*

In the synthesis of ditopic ligands, bispyrazolylpyridine molecules can be coupled with CH<sub>2</sub> linkages using sodium hydride and diiodomethane in dichloromethane with moderate yields, as reported by Zadykowicz and Potvin.<sup>13</sup>



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