

SYNLETT Spotlight 442

Diiodomethane: A Versatile C1 Building Block

Compiled by Cláudia Diana C. B. G. Raposo



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.¹ Being such an interesting compound, diiodomethane is a versatile C₁ 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,² diazotization,³

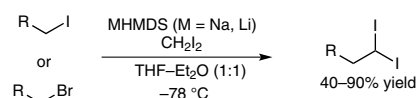
iodomethylation,⁴ cyclopropanation,⁵ alkene reduction,⁶ and sigmatropic rearrangement.⁷ In the presence of metallic samarium, the air-sensitive samarium diiodide (SmI₂) is formed in situ; this is cheaper than buying samarium diiodide.⁸

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.⁹

Abstracts

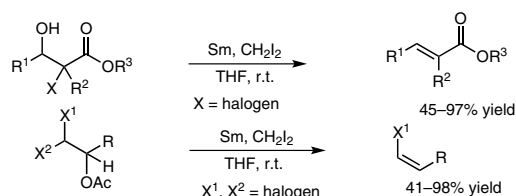
(A) Alkylation of Diiodomethane

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.¹⁰



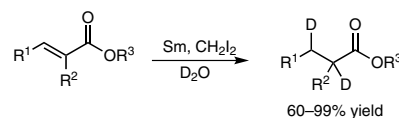
(B) β -Elimination of 2-Halogen-3-hydroxyesters and Synthesis of (Z)-Vinyl Halides

(*E*)- α,β -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-diodo alcohols, metallic samarium, and diiodomethane in THF at room temperature.⁸



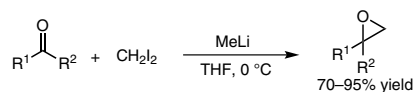
(C) Synthesis of 2,3-Dideuterioesters

The 1,4-reduction of α,β -unsaturated esters with D₂O in the presence of metallic samarium and diiodomethane afforded the corresponding 2,3-dideuterioesters in good to excellent yields.⁶



(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 methyl lithium at 0 °C.²



SYNLETT 2013, 24, 1737–1738

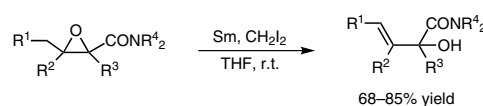
Advanced online publication: 17.07.2013

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

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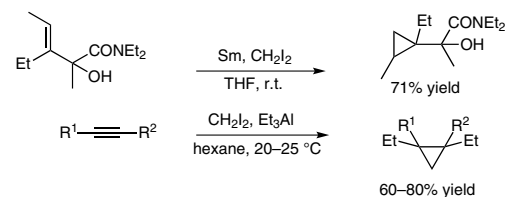
(E) Synthesis of (*E*)- α -Hydroxy- β,γ -unsaturated Amides

Concellón and co-workers¹¹ reported an easy and simple procedure to prepare (*E*)- α -hydroxy- β,γ -unsaturated amides using metallic samarium and diiodomethane with high regio- and diastereo-selectivity.



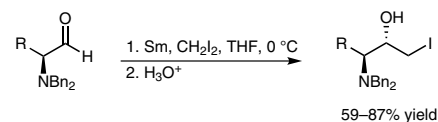
(F) Cyclopropanation

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



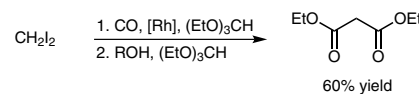
(G) Iodomethylation of Amino Aldehydes

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.⁴



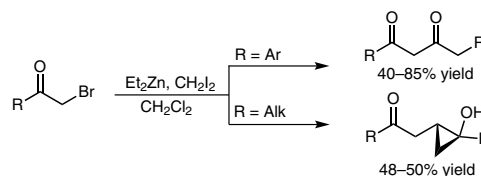
(H) Double Carbonylation of Diiodomethane

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



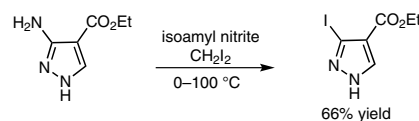
(I) Sigmatropic Rearrangement

Li and co-workers described an efficient method for the synthesis of β -diketones from aromatic α -bromo ketones in the presence of diiodomethane and diethylzinc. Aliphatic α -bromomethyl ketones gave 2,4-disubstituted furans or cyclopropanols in moderate yield.⁷

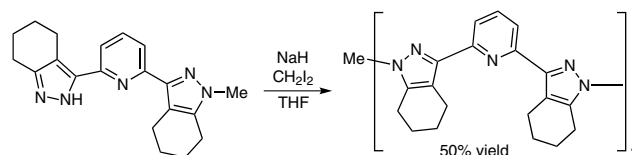


(J) Diazotization for the Synthesis of Aryl Iodides

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

(K) Coupling Molecules with a CH₂ Linkage

In the synthesis of ditopic ligands, bispyrazolylpyridine molecules can be coupled with CH₂ linkages using sodium hydride and diiodomethane in dichloromethane with moderate yields, as reported by Zadykovicz and Potvin.¹³



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