Diiodomethane: A Versatile C1 Building Block

Compiled by Cláudia Diana C. B. G. Raposo

Cláudia Raposo was born in Oeiras, Portugal in 1987. She received both her B.Sc. in Applied Chemistry and her M.Sc. in Bioorganic Chemistry from the Faculdade de Ciências e Tecnologia of Universidade Nova de Lisboa, Portugal, where she is currently working under the supervision of Dr. Krasimira Petrova. Her research is focused on carbohydrate synthesis and glucose-containing nanoparticles for targeted drug delivery.

REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
E-mail: piccfa@gmail.com

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-dioidoalkanes 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-functionalized systems. Concéllon 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
(E) Synthesis of (E)-α-Hydroxy-β,γ-unsaturated Amides
Concellón and co-workers\(^\text{11}\) reported an easy and simple procedure to prepare (E)-α-hydroxy-β,γ-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.\(^\text{11}\) Cyclopropanation of terminal alkynes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.\(^\text{6}\)

(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.\(^\text{4}\)

(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.\(^\text{2}\)

(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.\(^\text{7}\)

(J) Diazoitization for the Synthesis of Aryl Iodides
The reactions of aryl amines in the presence of isoamyl nitrite and H3O\(^+\) gave α-hydroxy-β-bromo ketones in the presence of diiodomethane and diethylzinc.\(^\text{12}\)

(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 Zadykowicz and Potvin.\(^\text{13}\)

References


