Diiodomethane: A Versatile C1 Building Block

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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 geological 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-Dideuteroesters
The 1,4-reduction of α,β-unsaturated esters with D2O in the presence of metallic samarium and diiodomethane afforded the corresponding 2,3-dideuteroesters 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-dirunctionalized systems. Conceição 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.2
(E) Synthesis of (E)-α-Hydroxy-β,γ-unsaturated Amides
Concellón and co-workers\(^1\) 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.\(^1\) Cyclopropanation of terminal alkenes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.\(^7\)

(G) Iodomethylation of Amino Aldehydes
The halomethylation of carbonyl compounds is difficult to achieve due to the instability of halomethylthium compounds. As an alternative, Bernad et al. reported an easy and simple procedure can be coupled with CH₂ linkages using sodium hydride and diiodomethane.\(^3\)

(H) Double Carboxylation of Diiodomethane
Double carboxylation 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) Diazaotization for the synthesis of Aryl Iodides
The reactions of aryl amines in the presence of isomyl 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 Zadykowicz and Potvin.\(^11\)

References
(9) Xu B., CN102020529-A, 2011.