**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 gemological industry to determine the density of minerals. It 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, diazotization, iodomethylation, cyclopropanation, alkene reduction, and sigmatropic rearrangement. In the presence of metallic samarium, the air-sensitive samarium diiodide (SmI₂) is formed in situ; this is cheaper than buying samarium diiodide.

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.

**Abstracts**

(A) **Alkylation of Diiodomethane**

Bull and Charette reported an improved procedure to obtain functionalized gem-diodoalkanes with acceptable functional group tolerance towards olefins, acetals, ethers, carbamates, and hindered esters.

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

(1R,2S)‐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.

(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.

(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 methylthium at 0 °C.
(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.\(^5\) Cyclopropanation of terminal alkynes under the action of diiodomethane and triethylaluminum proceeded stereoselectively.\(^6\)

(G) **Iodomethylation of Amino Aldehydes**

The halomethylation of carbonyl compounds is difficult to achieve due to the instability of halomethyllithium compounds. As an alternative, Bernad et al. reported a smoothly proceeding reaction using metallic samarium and diiodomethane.\(^4\) Double carbonylation of diiodomethane in triethylorthoformate in the presence of catalytic amounts of rhodium complex gave diethylmalonate from aromatic alkynes under the action of diiodomethane and triethylaluminum.\(^3\)

(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 diarylhydrazine. 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 hydrochloric acid gave aryl diazonium ions in moderate yields, as reported by Zadykowicz and Potvin.\(^13\)

(K) **Coupling Molecules with a CH₂ Linkage**


References