

Very Rapid Preparation of SmI₂ by Sonic Treatment of Iodoform and Metallic Samarium

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Keywords: Samarium / Sonication / Synthetic methods

A very rapid preparation of SmI₂ by sonication of a mixture of metallic samarium and iodoform in THF is described. To prove the synthetic applications of the obtained SmI₂ several high-yielding reactions were carried out. Preliminary results

for the generation of SmI₂ in THF by sonication from diiodomethane, 1,2-diiodoethane, or iodine are also described.

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Introduction

Since the pioneering studies of Kagan^[1] samarium diiodide has rapidly become an important reagent in synthetic organic chemistry because of its versatility in one- and two-electron-transfer reactions. Several reviews describing its applications in organic synthesis have been published.^[2]

Samarium diiodide can be prepared in moderate concentrations (0.1 M) in THF starting from samarium metal and diiodomethane, 1,2-diiodoethane or iodine. However, to the best of our knowledge, no method for the generation of SmI₂ has been described starting from iodoform.^[3]

A general method to prepare samarium diiodide using sound waves has also not been described.^[4] On the other hand, significant rate enhancements of chemical reactions have been described when heterogeneous reactions are carried out in the presence of sound waves.^[5]

Moreover, for synthetic purposes, SmI₂ is typically generated and utilised in situ. Based on our own experience and that of others, 1^[6] or 2^[7] h are required for the conventional generation of SmI₂ (from CH₂I₂, ICH₂CH₂I or I₂) and for this reason, a most rapid synthesis of SmI₂ would be very desirable.

In this communication we describe a very rapid synthesis of samarium diiodide in THF by ultrasonic irradiation of a mixture of metallic samarium and iodoform. This is the first synthesis of this reagent by this method and several organic reactions were carried out to prove the reactivity of the SmI₂ thus generated. We also describe the beneficial effects of faster reactions that ultrasonic irradiation has on the generation of SmI₂ from samarium and diiodomethane, 1,2-diiodoethane, or iodine.

Results and Discussion

We first investigated the generation of samarium diiodide from samarium and iodoform. This synthesis can be carried out by simple sonication of a mixture of samarium powder and iodoform in THF. After 5 min, a deep blue solution of SmI₂ was obtained (Scheme 1).



Scheme 1

This generation of SmI₂ was performed by using commercial products, without prior purification or activation. An iodine titration was in agreement with quantitative formation of samarium diiodide.

In comparison, preparation of SmI₂ by conventional treatment of iodoform with samarium (without ultrasonic irradiation), requires 3 h to complete the reaction. In this case, after 1 h only 48% and after 2 h 65% of SmI₂ (iodine titration) was obtained.

To prove the usefulness of the SmI₂ in THF prepared by sonication several transformations were performed: a β-elimination reaction from ethyl 2-methyl-3-(4-methoxyphenyl)-2,3-epoxypropanoate,^[8] a reduction reaction of sorbic acid in the presence of D₂O to the corresponding 2,5-dideuteriohex-3-enoic acid,^[9] a transformation of methyl cinnamate into methyl 2,3-dideuterio-3-phenylpropanoate,^[10] a pinacol coupling of benzaldehyde,^[11] a Reformatsky reaction between cyclohexanone and ethyl 2-bromopropanoate,^[12] and a carbon–carbon bond formation by a Barbier-type reaction.^[13] The results are summarised in Table 1.

Taking into account the preceding results, we investigated the effects that ultrasonic irradiation has on the generation

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Table 1. Organic transformations carried out by CHI_3 generated SmI_2

Entry	Starting Compounds	Product	Yield (%) ^[a]
1			85
2			88
3			97
4			95
5			97

^[a] Isolated yield based on the starting compound; all obtained compounds were fully characterized by spectroscopic methods (IR, NMR, and MS) and when possible compared with the spectroscopic data previously described.

of SmI_2 starting from conventionally used iodo compounds (CH_2I_2 , $\text{ICH}_2\text{CH}_2\text{I}$ or I_2). Here we described the preliminary results. Thus, the sonication of a mixture of samarium and diiodomethane in THF rapidly afforded a deep blue solution of SmI_2 (5–10 min). This solution was used to carry out a β -elimination reaction (Table 2, Entry 1) and a diiodomethylation of an aldehyde (Table 2, Entry 2).

In the same way, the sonication of a mixture of samarium and 1,2-diiodoethane in THF afforded a deep blue solution of SmI_2 in a short reaction time (10 min). This solution was used to perform the coupling of an α,β -unsaturated ester and an aldehyde^[14] and the transformation of an acid chloride into an α -diketone,^[15] (Table 2, Entries 3 and 4).

Ultrasonic irradiation also has beneficial effects on the generation of SmI_2 in THF from iodine. The THF solution of SmI_2 obtained was used to transform cyclohexanone into 1-iodomethylcyclohexan-1-ol,^[16] (Table 2, Entry 5).

All products were obtained in similar or higher yields to those previously reported.

This preparation of samarium diiodide by using ultrasonic irradiation has several advantages in comparison to conventional methodology: a) activation of samarium powder by heating is not necessary; b) addition of THF and the corresponding iodo compound is carried out in one portion; c) commercial iodo compounds (without purification) can be used, and d) the reaction time is considerably shorter.

Table 2. Organic transformations carried out with SmI_2 generated from diiodomethane, 1,2-diiodoethane, and iodine

Entry	Starting Compounds	Product	Yield (%) ^[a]
1 ^[b]			91
2 ^[b]			56
3 ^[c]			98
4 ^[c]			71
5 ^[d]			81

^[a] Isolated yield based on the starting compound; all obtained compounds were fully characterized by spectroscopic methods (IR, NMR, and MS) and when possible compared with the spectroscopic data previously described. ^[b] SmI_2 was generated from samarium and diiodomethane. ^[c] SmI_2 was generated from samarium and 1,2-diiodoethane. ^[d] SmI_2 was generated from samarium and iodine.

Conclusion

In conclusion we have described the first synthesis of samarium diiodide in THF by using samarium and iodoform. This preparation, by ultrasonic irradiation of a mixture of samarium powder and iodoform, is very rapid, simple, and easy. The reactivity of SmI_2 prepared in this way is similar to the conventionally prepared material starting from other iodo compounds. Preliminary results of the sonical synthesis of SmI_2 in THF from diiodomethane, 1,2-diiodoethane, and iodine, are presented. Work is underway to prepare SmBr_2 in THF and SmI_2 in solvents other than THF employing sound waves.

Experimental section

General Remarks: Reactions requiring an inert gas were conducted under dry nitrogen, and the glassware was oven-dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the highest quality available and were used without further purification. ^1H NMR spectra were recorded at 200, 300, or 400 MHz. ^{13}C NMR spectra and DEPT experiments were determined at 50, 75, or 100 MHz. GC-MS and HRMS were measured at 70 eV. Chemical shifts are given in δ (ppm) relative to TMS as internal standard in the case of ^1H NMR spectra and relative to CDCl_3 in the case of ^{13}C NMR spectra.

Synthesis of SmI₂ by Sonication of Samarium Powder and Iodoform: Samarium powder (0.172 g, 1.1 mmol) was placed in a Schlenk tube at room temperature and dry THF (12 mL) was added. The Schlenk tube was then partially submerged to the solvent level in a conventional cleaner sonicator (ultrasound laboratory cleaner 230 V, 150 W, 50 Hz) and iodoform (0.27 g, 0.7 mmol) was added. After 5 min, a deep blue solution of SmI₂ was obtained.

Ethyl (*E*)-2-Methyl-3-(4-methoxyphenyl)propenoate (1a): A solution of SmI₂ (1.6 mmol) in THF (19 mL) was added dropwise, under nitrogen, to a stirred solution of ethyl 2-methyl-3-(4-methoxyphenyl)-2,3-epoxypropanoate (0.094 g, 0.4 mmol) in THF (4 mL) at room temperature. The reaction mixture was stirred for 90 min, and then quenched with aqueous HCl (0.1 M). Usual workup afforded the crude (*E*)- α,β -unsaturated ester which was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 10:1). Yield: 74.8 mg (85%). ¹H NMR (300 MHz, CDCl₃): δ = 1.33 (t, *J* = 7.1 Hz, 3 H), 2.12 (s, 3 H), 3.80 (s, 3 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 6.89 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.60 (s, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 13.9 (CH₃), 14.2 (CH₃), 55.0 (CH₃), 60.6 (CH₂), 113.6 (CH), 126.1 (C), 128.3 (C), 131.2 (CH), 138.2 (CH), 159.4 (C), 168.8 (C) ppm. MS (70 eV): *m/z* (%) = 220 [M⁺] (100), 191 (32), 175 (85), 147 (83). IR: $\tilde{\nu}$ = 2975, 1702, 1605 cm⁻¹. *R_f* = 0.4 (hexane/EtOAc, 5:1).

(*E*)-2,5-Dideuteriohex-3-enoic Acid (1b): Under nitrogen, a solution of SmI₂ (1.2 mmol) in THF (15 mL) was added dropwise to a stirred solution of sorbic acid in D₂O (2 mL) and THF (2 mL) at room temperature. The reaction mixture was stirred for 30 min and then treated with 0.1 M aqueous HCl. Standard workup afforded the crude dideuterioacid, which was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 5:1). Yield: 40.6 mg (88%). ¹H NMR (300 MHz, CDCl₃): δ = 0.99 (d, *J* = 7.4 Hz, 3 H), 1.99–2.09 (m, 1 H), 3.03–3.08 (m, 1 H), 5.50 (dd, *J* = 15.2, 5.9 Hz, 1 H), 6.65 (dd, *J* = 15.2, 5.3 Hz, 1 H), 10.46 (br. s, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 13.2 (CH₃), 25.1 (t, *J* = 19.4 Hz, CHD), 37.5 (t, *J* = 19.5 Hz, CHD), 119.7 (CH), 136.8 (CH), 178.7 (C) ppm. MS (70 eV): *m/z* (%) = 116 (63) [M⁺], 70 (63), 56 (100), 42 (85). HRMS: calcd. for C₆H₈D₂O₂ 116.0804, found 116.0810. IR: $\tilde{\nu}$ = 3325, 2964, 1713 cm⁻¹. *R_f* = 0.5 (hexane/EtOAc, 3:1).

Methyl 2,3-Dideuterio-3-phenylpropanoate (1c): Successive treatment of methyl cinnamate (0.065 g, 0.4 mmol) in THF (2 mL) with SmI₂ (1.1 mmol) in THF (12 mL) for 30 min, at room temperature, and then with D₂O (2 mL) over a period of 30 min, afforded methyl 2,3-dideuterio-3-phenylpropanoate which was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 10:1). Yield: 64.7 mg (97%). ¹H NMR (300 MHz, CDCl₃): δ = 2.63 (d, *J* = 8.3 Hz, 1 H), 2.94 (d, *J* = 8.3 Hz, 1 H), 3.68 (s, 3 H), 7.19–7.33 (m, 5 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 30.5 (t, *J* = 19.8 Hz, CHD), 35.2 (t, *J* = 19.8 Hz, CHD), 51.5 (CH₃), 126.2 (CH), 128.2 (CH), 128.4 (CH), 140.3 (C), 173.3 (C) ppm. MS (70 eV): *m/z* (%) = 166 (40) [M⁺], 135 (12), 107 (37), 106 (100), 92 (65). IR: $\tilde{\nu}$ = 3085, 3027, 2958, 1738, 1496, 1435 cm⁻¹. *R_f* = 0.3 (hexane/EtOAc, 10:1).

1,2-Diphenylethanediol (1d): Benzaldehyde (0.08 mL, 2 mmol), dissolved in THF (5 mL), was added at room temperature under nitrogen, to a 0.1 M solution of SmI₂ in THF (20 mL, 2 mmol). The typical blue color of SmI₂ immediately turned orange. After stirring for 10 min, a yellow precipitate appeared. Hydrolysis with 0.1 M HCl, followed by diethyl ether extraction and washing of the extract with sodium thiosulfate and saturated NaCl solution gave the corresponding pinacol. Yield: 203.3 mg (95%). ¹H NMR

(200 MHz, CDCl₃): δ = 4.0 (br. s, 2 H), 4.70 ($\pm$) (s, 2 H), 4.80 (*meso*), 6.9–7.4 (m, 10 H). ¹³C NMR (50 MHz, CDCl₃): δ = 77.6 (CH), 78.9 (CH), 126.9 (CH), 127.6 (CH), 127.7 (CH), 128.2 (CH), 129.9 (CH), 133.3 (CH), 139.6 (C), 139.7 (C) ppm. IR: $\tilde{\nu}$ = 3390, 1950, 1884, 1682, 1602, 1584, 1494, 1453, 1022 cm⁻¹. *R_f* = 0.4 (hexane/EtOAc, 10:1).

Ethyl 2-(1-Hydroxycyclohexyl)propionate (1e): To a THF solution of SmI₂ (2 mmol) was added a solution of cyclohexanone (0.10 mL, 1 mmol) in THF (5 mL) and then ethyl 2-bromopropanoate (0.13 mL, 1 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 10 min and then quenched with aqueous HCl (0.1 M). Usual workup and purification by column flash chromatography provided the pure β -hydroxy ester. Yield: 194.0 mg (97%). ¹H NMR (200 MHz, CDCl₃): δ = 1.13 (d, *J* = 7.2 Hz, 3 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.40–1.60 (m, 10 H), 2.43 (q, *J* = 7.2 Hz, 1 H), 3.01 (br. s, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 11.3 (CH₃), 13.9 (CH₃), 21.4 (CH₂), 21.7 (CH₂), 25.5 (CH₂), 33.6 (CH₂), 36.7 (CH₂), 47.7 (CH), 60.2 (CH₂), 71.1 (C), 176.8 (C) ppm. MS (70 eV): *m/z* (%) = 200 (2) [M⁺], 157 (35), 144 (29), 111 (18), 102 (100), 99 (59), 98 (30), 81 (62), 74 (61), 56 (46), 55 (57), 45 (24), 43 (45), 41 (49). IR: $\tilde{\nu}$ = 3441, 2936, 2862, 1712, 1636, 1457, 1373, 1334, 1260, 1183, 1097, 1049, 961 cm⁻¹. *R_f* = 0.4 (hexane/EtOAc, 5:1).

Synthesis of SmI₂ by Sonication of a Mixture of Samarium Powder and Diiodomethane: The sonication of samarium powder (0.172 g, 1.1 mmol) and diiodomethane (0.08 mL, 1.1 mmol) in THF (12 mL) at room temperature for 5–10 min afforded a deep blue solution of SmI₂.

(*E*)-*N,N*-Diethyl-4-phenylpent-2-enamide (1f): A solution of SmI₂ (1 mmol) in THF (12 mL) was added very slowly dropwise, under nitrogen, to a stirred solution of 2-chloro-*N,N*-diethyl-3-hydroxy-4-phenylpentanamide (0.104 g, 0.4 mmol) in THF (2 mL) at room temperature. After 30 min, the reaction was quenched with aqueous HCl (1 M). Usual workup provided the crude α,β -unsaturated amide, which was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 3:1) to provide the pure compound. Yield: 83.2 mg (91%). ¹H NMR (300 MHz, CDCl₃): δ = 0.94–1.32 (m, 6 H), 1.43 (d, *J* = 7.0 Hz, 3 H), 3.32 (q, *J* = 7.0 Hz, 2 H), 3.41 (q, *J* = 7.0 Hz, 2 H), 3.65–3.68 (m, 1 H), 6.13 (d, *J* = 15.2 Hz, 1 H), 7.07 (dd, *J* = 15.2, 7.0 Hz, 1 H), 7.20–7.33 (m, 5 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 13.0 (CH₃), 14.7 (CH₃), 20.7 (CH₃), 40.7 (CH₂), 42.1 (CH₂), 42.1 (CH), 119.3 (CH), 126.4 (CH), 127.2 (CH), 128.4 (CH), 143.9 (C), 149.5 (CH), 165.7 (C) ppm. MS (70 eV): *m/z* (%) = 231 (89) [M⁺], 159 (92), 131 (85), 126 (100), 91 (81), 77 (36). HRMS: calcd. for C₁₅H₂₁NO 231.1623, found 231.1627. IR: $\tilde{\nu}$ = 3008, 2945, 1647 cm⁻¹. *R_f* = 0.1 (hexane/EtOAc, 5:1).

1,1-Diiodononan-2-ol (1g): To a solution of octanal (0.078 mL, 0.5 mmol) and iodoform (0.4 g, 1 mmol) in THF (18 mL) was added dropwise, under nitrogen, SmI₂ (2 mmol) at 0 °C. The mixture was stirred for 45 min and then was quenched by addition of aqueous HCl (0.1 M). Usual workup afforded the crude diiodo alcohol which was purified by flash column chromatography on silica gel (polarity gradient, from hexane to hexane/ethyl acetate, 10:1). Yield: 110.9 mg (56%). ¹H NMR (200 MHz, CDCl₃): δ = 0.87 (m, 3 H), 1.18–1.74 (m, 12 H), 2.40 (br. s, 1 H), 3.15 (br. s, 1 H), 5.28 (d, *J* = 3.0 Hz, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = -9.4 (CH), 14.0 (CH₃), 22.5 (CH₂), 25.3 (CH₂), 29.0 (CH₂), 29.3 (CH₂), 31.6 (CH₂), 36.0 (CH₂), 77.3 (CH) ppm. MS (70 eV): *m/z* (%) = 396 [M⁺] (15), 269 (48), 170 (40), 123 (56), 81 (100), 55 (60), 41 (74). HRMS: calcd. for C₉H₁₈I₂O 395.9447, found 395.9449. IR:

$\tilde{\nu}$ = 3402, 3410, 2924, 1076, 1464 cm^{-1} . R_f = 0.3 (hexane/EtOAc, 10:1).

Preparation of SmI_2 by Sonication of a Mixture of Samarium Powder and 1,2-Diiodoethane: Samarium powder (0.275 g, 1.6 mmol) was placed in a Schlenk tube at room temperature with 1,2-diiodoethane (0.451 g, 1.6 mmol) and then dry THF (20 mL) was added. The Schlenk tube was partially submerged to the solvent level in the sonicator. After sonication for 15 min, a deep blue solution of SmI_2 was obtained.

2-Cyclohexyl-4-methyloxolan-2-one (1h): A solution of SmI_2 (3 mmol) in THF (30 mL) was added dropwise, under nitrogen, to a stirred solution of cyclohexanecarboxaldehyde (0.12 mL, 1 mmol), methyl but-2-enoate (0.214 mL, 2 mmol), 2-propanol (0.11 mL, 1.5 mmol) and HMPA (1 mL) in THF (2 mL) at 0 °C. The reaction mixture was stirred for 1 min, and then quenched with aqueous HCl (0.1 M). Usual workup and purification by flash column chromatography provided the pure lactone. Yield: 178.4 mg (98%). ^1H NMR (200 MHz, CDCl_3): δ = 0.93 (d, J = 6.8 Hz, 3 H), 1.08 (d, J = 6.8 Hz, 3 H), 0.80–1.31 (m, 10 H), 1.41–1.82 (m, 10 H), 1.89–2.73 (m, 8 H), 3.61–3.99 (m, 2 H), ^{13}C NMR (75 MHz, CDCl_3): δ = 13.1 (CH_3), 18.9 (CH_3), 25.0 (CH_2), 25.5 (CH_2), 25.7 (CH_2), 26.0 (CH_2), 27.5 (CH_2), 38.4 (CH_2), 27.6 (CH_2), 28.7 (CH_2), 30.0 (CH_2), 31.6 (CH), 31.9 (CH), 36.8 (CH_2), 37.1 (CH), 41.3 (CH), 87.1 (CH), 90.9 (CH), 176.3 (C), 176.4 (C) ppm. MS (70 eV): m/z (%) = 182 (> 1) [M^+], 99 (33), 83 (16), 41 (100). IR: $\tilde{\nu}$ = 2922, 1773, 1450, 1171 cm^{-1} . R_f = 0.2 (hexane/EtOAc, 5:1).

Diphenylethanedione (1i): A solution of benzoyl chloride (0.09 mL, 0.8 mmol) in THF (2 mL) was slowly added under nitrogen at room temperature to 1.6 mmol of 0.1 M SmI_2 solution in THF. This solution turned yellow in a few minutes. Dilute HCl was then added. After diethyl ether extraction, washing with aqueous NaHCO_3 , and drying with sodium sulfate, the α -diketone **1i** was recovered after recrystallization. Yield: 58.8 mg (71%). ^1H NMR (200 MHz, CDCl_3): δ = 7.28–8.21 (m, 10 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 128.9 (CH), 129.8 (CH), 132.9 (C), 134.8 (CH), 194.5 (C) ppm. MS (70 eV): m/z (%) = 210 (5) [M^+], 105 (100), 77 (76), 51 (35). IR: $\tilde{\nu}$ = 3061, 1682, 1596, 1449, 1265, 1211 cm^{-1} . R_f = 0.4 (hexane/EtOAc, 5:1).

Synthesis of SmI_2 by Sonication of Samarium Powder and Iodine: Samarium powder (0.172 g, 1.1 mmol) was placed in a Schlenk tube at room temperature with iodine (0.25 g, 1 mmol) and then dry THF (10 mL) was added. The Schlenk tube was partially submerged to the solvent level in the sonicator. After sonication for 1 h, a deep blue solution of SmI_2 was obtained.

1-Iodomethylcyclohexanol (1j): A solution of SmI_2 (2.5 mmol) in THF (25 mL) was added dropwise, under nitrogen, to a stirred solution of cyclohexanone (0.10 mL, 1 mmol) and diiodomethane (0.16 mL, 2 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 3 min, after which time the blue-green color had turned to yellow. The reaction was then quenched with aqueous HCl (0.1 M). Usual workup and purification by flash column chromatography provided the iodo alcohol. Yield: 194.4 mg (81%). ^1H NMR (200 MHz, CDCl_3): δ = 1.07–2.05 (m, 10 H), 3.32 (s, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 21.2 (CH_2), 24.6 (CH_2), 25.3 (CH_2), 36.4 (CH_2), 68.9 (C) ppm. MS (70 eV): m/z (%) = 240 (9) [M^+], 127 (14), 113 (27), 99 (100). IR: $\tilde{\nu}$ = 3418, 2931, 1446, 978 cm^{-1} . R_f = 0.4 (hexane/EtOAc, 3:1).

Acknowledgments

We thank III Plan Regional de Investigación del Principado de Asturias (PB-EXP01-11) and Ministerio de Educación y Cultura (BQU2001-3807) for financial support. J. M. C. thanks Carmen Fernández-Flórez for her time. H. R. S. and E. B. thank Principado de Asturias and M. H. the Ministerio de Ciencia, Cultura y Deportes for a predoctoral fellowship. Robin Walker revised the English of the manuscript.

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Received November 29, 2002