

Reactions of diaryliodonium trifluoromethanesulfonates with low-valent ytterbium and samarium reagents

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Abstract

The reduction of diaryliodonium trifluoromethanesulfonates with low-valent ytterbium and samarium reagents has been studied. In the reaction of diphenyliodonium trifluoromethanesulfonate with two equimolar amounts of metallic ytterbium, benzene is formed almost quantitatively. On the other hand, iodobenzene is produced together with benzene in the reaction with divalent YbI_2 or SmI_2 . The intermediates generated in situ by the reaction of arylphenyliodonium trifluoromethanesulfonates and metallic ytterbium are trapped with methylphenylsilane to afford diphenylmethylsilane and arylmethylphenylsilanes. With respect to the substituent effect on the aromatic ring of the arylphenyliodonium salts, electron-donating groups favor the formation of arylmethylphenylsilanes rather than diphenylmethylsilane, whereas electron-withdrawing groups induce the favorable production of diphenylmethylsilane. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hypervalent iodine compounds have become of great interest in recent years owing to their biological and chemical uniqueness [1]. Among them, diaryliodonium salts can be regarded as precursors of aryl carbocations and utilized in the reactions coupling with various nucleophiles. Diaryliodonium salts exhibit another aspect of an electron acceptor, and the photochemical [2] and electrochemical [3] reductions of diaryliodonium salts have been well documented. However, much less has been reported on the reactions of diaryliodonium salts with low-valent metallic reductants [4]. In particular, to the best of our knowledge no publications have dealt with lanthanoid induced reductions of diaryliodonium salts in spite of their strong reducing power [5]. We have established synthetic reactions induced by lanthanoid metals and revealed their unique reactivity of organolanthanoid(II) iodides to hydrosilanes and carbonyl compounds [6]. Thus, the combination of those oxidants and low-valent lanthanoid reductants

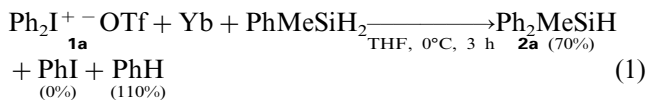
naturally arouse our interest. Herein we wish to report on the chemical behavior of diaryliodonium trifluoromethanesulfonates with low-valent lanthanoid reductants.

2. Results and discussion

The reaction of diphenyliodonium trifluoromethanesulfonate (**1a**) (0.50 mmol) with zerovalent Yb (40 mesh, 1.0 mmol) in THF at 0°C for 1 h gave 0.99 mmol (199%) of benzene. However, either iodobenzene or phenyl trifluoromethanesulfonate was not produced. When a similar reaction was carried out in the presence of methylphenylsilane (2.0 mmol) for 12 h, diphenylmethylsilane (**2a**) (0.35 mmol, 70%) was produced (70%) together with benzene (0.55 mmol, 110%) (Eq. (1)). On the other hand, the reaction of **1a** with Yb at 0°C for 1 h, followed by treating with cyclohexanone (1.0 mmol) afforded 1-phenylcyclohexanol (**3**) (0.32 mmol) in 65% yield. These results are the evidence supporting that phenyl ytterbium species whose phenyl moiety is anionic are in situ formed by the electron transfer from low-valent ytterbium to **1a**.

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Other lanthanoid reducing agents were also tested for the reaction of the diaryliodonium salt **1a**. Using zerovalent samarium in lieu of ytterbium resulted in no reaction. In the case of YbI_2 [7], a divalent ytterbium, which acts as a one-electron reductant in various transformations of organic functional groups [8,9], benzene and iodobenzene were produced in 99 and 79% yields, respectively. SmI_2 [7] also reduced **1a** to give benzene (94%) and iodobenzene (92%). However, no formation

Table 1

Influence of the amounts of Yb on the product distribution in the reaction of diphenyliodonium trifluoromethanesulfonate (**1a**) with Yb and PhMeSiH_2

Entry	Yb (equivalent to 1a)	Yields (%) ^a		
		Ph_2MeSiH	PhI	PhH
1	2.0	70	0	110
2	1.0	30	34	126
3	0.66	18	48	122
4	0.33	7	66	100

^a GC yields.

Table 2

Reaction of arylphenyliodonium trifluoromethanesulfonates **1** with Yb in the presence of PhMeSiH_2

Entry	ArPhI ⁺ OTf ⁻ , Ar	Yields (%) ^a	
		Ph_2MeSiH	ArPhMeSiH
1	Ph (1a)	70 (2a)	^a
2	<i>p</i> -MeC ₆ H ₄ (1b)	24 (2a)	42 (2b)
3	<i>p</i> -MeOC ₆ H ₄ (1c)	14 (2a)	21 (2c)
4	<i>p</i> -ClC ₆ H ₄ (1d)	31 (2a)	15 (2d)
5	2,4,6-Me ₃ C ₆ H ₂ (1e)	12 (2a)	^b
6	2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ (1f)	28 (2a)	^c

^a GC yields.

^b 2,4,6-Me₃C₆H₂I was formed in 59% yield.

^c 2,4,6-*i*-Pr₃C₆H₂I was formed in 28% yield.

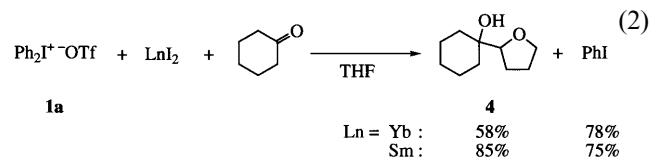
Table 3

Reduction of ArPhIOTf **1** with ytterbium (0.33 equivalents)

Entry	Iodonium salt, Ar	Yields (%) ^a			
		PhH	ArH	PhI	ArI
1	Ph (1a)	80	–	76	–
2	<i>p</i> -MeC ₆ H ₄ (1b)	47	29	27	50
3	<i>p</i> -MeOC ₆ H ₄ (1c)	59	26	21	59
4	<i>p</i> -ClC ₆ H ₄ (1d)	21	65	58	19
5	2,4,6-Me ₃ C ₆ H ₂ (1e)	67	21	17	68
6	2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ (1f)	28	60	47	37

^a GC yields.

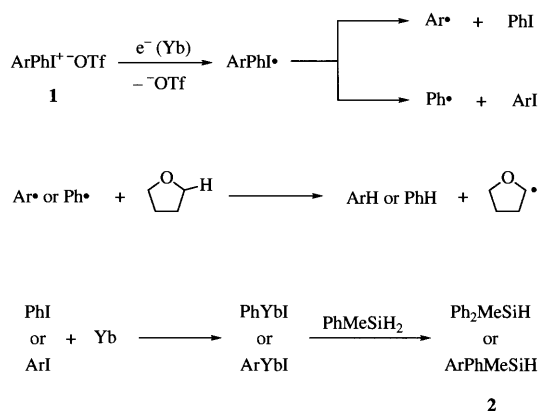
of Ph_2MeSiH (**2a**) could be observed when MePhSiH_2 was present in those two reactions. Instead, the reaction of **1a** with YbI_2 or SmI_2 in the presence of cyclohexanone afforded the alcohol **4** in 58 and 85%, respectively (Eq. (2)).



As Ph_2MeSiH (**2a**) was formed in the reaction of **1a** with excess Yb in the presence of MePhSiH_2 , the effect of the amounts of Yb on the product distribution was investigated (Table 1). As mentioned above, **2a** was obtained together with benzene when two equivalents of Yb were treated with **1a**, but no iodobenzene could be detected on GC (Entry 1). On the contrary, iodobenzene was produced in 34% yield in the reaction with an equimolar amount of Yb (Entry 3). Table 1 indicates that decreasing the amount of Yb causes the decrease in the yield of **2a** and the increase of iodobenzene. However, production of benzene seems to be independent on the variation of the amount of Yb. A similar phenomenon was observed in the trapping experiment with a ketone. The reaction of **1a** with one equivalent of Yb, followed by trapping with cyclohexanone gave **4** and iodobenzene in 38 and 38% yields, respectively.

Next, the reaction of arylphenyliodonium salts **1a–d** with Yb in the presence of MePhSiH_2 were performed in order to investigate the relationship between the substituent of **1** and the selectivity of the products. The results are summarized in Table 2. In all reactions, neither iodobenzene nor aryl iodides could be detected on GC. In the reaction of phenyl(*p*-tolyl)iodonium- (**1b**) and *p*-anisylphenyliodonium trifluoromethanesulfonates (**1c**), which have electron donating groups on the aromatic rings, *p*-tolyl- and *p*-anisyl-substituted monohydrosilanes **2b** and **2c** were predominantly produced (Entries 2 and 3). On the other hand, **2a** was afforded in superior yield compared with (*p*-ClC₆H₄) PhMeSiH (**2d**), which contains an electron-withdrawing group (Entry 4). Although mesitylphenyliodonium- and phenyl(2,4,6-triisopropylphenyl)iodonium salts **1e** and **1f** reacted with metallic ytterbium, only **2a** was produced in 12 and 28% yields, respectively, as the silylated products (Entries 5 and 6). In addition, iodomesitylene (59%) and 1-iodo-2,4,6-triisopropylbenzene (28%) were formed.

To investigate the pathway for the formation of monohydrosilanes **2**, the reductions of **1a–d** with a 0.33 equivalents of Yb were examined (Table 3). In these reactions, PhH, ArH, PhI, and ArI were produced. With respect to the production of PhH and ArH, the yields of ArH were less than those of PhH in the reaction of **1b** and **1c** (Entries 2 and 3), whereas



Scheme 1.

chlorobenzene was predominantly formed in the reaction of **1d** (Entry 4). In contrast, an opposite tendency was observed for the yield of PhI and ArI; the reactions of **1b** and **1c** gave ArI in better yields than PhI (Entries 2 and 3), whereas the reaction of **1d** produced more yield of PhI than that of 4-chloriodobenzene (Entry 4). Formation of ArH and PhI was superior in the reduction of sterically hindered **1f** (Entry 6). The PhI:ArI ratios are in good agreement with the reported data of the electrochemical one-electron reduction of arylphenyliodonium bromides at mercury cathodes [3a] and the CrCl₂-induced reductive coupling of arylphenyliodonium tetrafluoroborates and benzaldehydes [4].

The first stage of the reactions of **1** with metallic ytterbium should be the one-electron transfer from zero- or divalent ytterbium to **1** to generate [9-I-2] arylphenyliodonium radicals [3,4], leading to Ar• and PhI or to Ph• and ArI (Scheme 1). Since the alcohol **4** was produced from the reduction of **1a** with LnI₂ (Ln = Sm or Yb) [10], phenyl and aryl radicals should abstract a hydrogen atom from THF to give benzene and ArH together with a trihydrofuryl radical. However, the fate of the trihydrofuryl radical, which is formed in the reaction of **1** with lanthanoid reductants in the absence of cyclohexanone, is still unknown. The further one-electron reduction of phenyl or aryl radicals with divalent ytterbium species to give phenyl and aryl anions can be neglected because **2a** was not formed from the reaction of **1a** with YbI₂ or SmI₂.

On the other hand, no reaction occurred when iodobenzene was treated with divalent YbI₂ [7]. In addition, the predominant formation of the more electron donating arylmethylphenylsilanes (Table 2) is closely related to the preferential production of ArI contains electron donating groups (Table 3) affects. It is reasonable to consider that the second stage is the two-electron transfer from zerovalent ytterbium to aryl iodides to generate phenyl- and arylytterbium iodides [11], which undergo phenylation or arylation of methylphenylsilane to give **2a–d** [6a].

In summary, we first investigated the chemical behavior of diaryliodonium trifluoromethanesulfonates towards low-valent lanthanoids and revealed that two kinds of reduction occur stepwise. Synthetic application of diaryliodonium salt/lanthanoid reagents is currently under way.

3. Experimental

3.1. Measurements and materials

Melting points were determined with a Yanaco melting point apparatus and are uncorrected. ¹H- and ¹³C-NMR spectra were recorded on a JEOL JNM-AL300 spectrometer, and chemical shifts were expressed in δ ppm downfield from tetramethylsilane. IR spectra were recorded on a HORIBA FT-200 IR spectrophotometer. Analytical GC evaluations of product mixtures were performed on a Shimadzu GC-9A flame ionization chromatograph. Elemental analyses were performed by the Service of the Elementary Analysis of Organic Compounds, Graduate School of Science, Kyushu University.

All reactions were performed under argon. THF was distilled from sodium/benzophenone. Ytterbium (40 mesh) was washed with THF and dried under vacuum. Arylphenyliodonium trifluoromethanesulfonates [12] and lanthanoid(II) iodides [7] were prepared according to the literature method. Other materials were commercially available and used without further purification.

3.2. General procedure for the reduction of arylphenyliodonium trifluoromethanesulfonates with ytterbium in the presence of phenylmethylsilane

An arylphenyliodonium trifluoromethanesulfonate **1** (0.50 mmol) was added into a 30 ml Schlenk tube containing ytterbium (173 mg, 1.0 mmol), THF (3 ml) and methylphenylsilane (244 mg, 2.0 mmol) at 0°C. The mixture was stirred for 3 h at 0°C, followed by addition of 0.1 ml of water. After *n*-eicosane as an internal standard was added to the resulting mixture, the mixture was analyzed by GC to qualify and quantify the products. Separation of the products was performed by column chromatography on SiO₂, using *n*-hexane as an eluent.

Diphenylmethylsilane (**2a**): colorless liquid. IR (neat) 2121.3, 1261.2 cm⁻¹; ¹H-NMR (CDCl₃): δ 0.62 (d, *J* = 4.0 Hz, 3H), 4.94 (q, *J* = 4.0 Hz, 1H), 7.32–7.39 (m, 6H), 7.53–7.58 (m, 4H); ¹³C-NMR (CDCl₃): δ -5.0, 127.9, 129.5, 134.8, 135.3. These spectra are in good agreement with those of the authentic sample commercially available.

Methyl(4-methylphenyl)phenylsilane (**2b**): colorless liquid. IR (neat) 2119.4, 1249.5 cm⁻¹; ¹H-NMR

(CDCl₃): δ 0.60 (d, $J = 3.6$ Hz, 3H), 2.35 (s, 3H), 4.92 (q, $J = 3.6$ Hz, 1H), 7.19 (d, $J = 7.5$ Hz, 2H), 7.34–7.36 (m, 3H), 7.45 (d, $J = 3.6$ Hz, 2H), 7.54–7.56 (m, 2H); ¹³C-NMR (CDCl₃): δ -4.9, 21.5, 127.9, 128.8, 129.4, 131.6, 134.8, 134.9, 135.6, 139.5. Anal. Calc. for C₁₄H₁₆Si: C, 79.18; H, 7.59. Found: C, 79.30; H, 7.63%.

(4-Methoxyphenyl)methylphenylsilane (**2c**): colorless liquid. IR (neat) 2834.8, 2117.5, 1249.6 cm⁻¹; ¹H-NMR (CDCl₃): δ 0.59 (d, $J = 4.0$ Hz, 3H), 3.81 (s, 3H), 4.92 (q, $J = 4.0$ Hz, 1H), 6.92 (d, $J = 8.6$ Hz, 2H), 7.35–7.37 (m, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.53–7.56 (m, 3H); ¹³C-NMR (CDCl₃): δ -4.8, 55.0, 113.8, 126.0, 127.9, 129.4, 134.8, 135.8, 136.3, 160.8. Anal. Calc. for C₁₄H₁₆OSi: C, 73.63; H, 7.06. Found: C, 73.76; H, 7.24%.

(4-Chlorophenyl)methylphenylsilane (**2d**): colorless liquid. IR (neat) 2125.2, 1253.5 cm⁻¹; ¹H-NMR (CDCl₃): δ 0.61 (d, $J = 3.6$ Hz, 3H), 4.92 (q, $J = 3.6$ Hz, 1H), 7.32–7.54 (m, 9H); ¹³C-NMR (CDCl₃): δ -5.1, 128.1, 128.2, 129.7, 133.7, 134.7, 135.9, 136.2. Anal. Calc. for C₁₃H₁₃ClSi: C, 67.08; H, 5.63. Found: C, 66.82; H, 5.66%.

Iodomesitylene [14]: colorless needles; m.p. 29.8–30.8°C (Lit. [14] 30–31°C). IR (neat) 2921.6, 1457.9, 1004.7, 846.6 cm⁻¹; ¹H-NMR (CDCl₃): δ 2.22 (s, 3H), 2.42 (s, 6H), 6.87 (s, 2H); ¹³C-NMR (CDCl₃): δ 20.6, 29.5, 104.2, 127.9, 137.2, 141.7.

1-Iodo-2,4,6-triisopropylbenzene [14]: colorless oil. IR (neat) 2960.2, 1461.8, 998.9, 873.6 cm⁻¹; ¹H-NMR (CDCl₃): δ 1.24 (d, $J = 6.9$ Hz, 12H), 1.25 (d, $J = 6.9$ Hz, 6H), 2.87 (sep, $J = 6.9$ Hz, 1H), 3.39 (sep, $J = 6.9$ Hz, 2H), 6.95 (s, 2H); ¹³C-NMR (CDCl₃) δ 23.4, 24.0, 33.9, 39.2, 105.6, 122.0, 148.8, 150.7.

3.3. Reaction of diphenyliodonium trifluoromethanesulfonate with ytterbium and cyclohexanone

Diphenyliodonium trifluoromethanesulfonate (**1a**) (216 mg, 0.50 mmol) was added into a 30 ml Schlenk tube containing ytterbium (173 mg, 1.0 mmol) and THF (3 ml) at 0°C. The mixture was stirred for 1 h, then cyclohexanone (98 mg, 1.0 mmol) was added, and the mixture was stirred for a further 0.5 h. The resulting mixture was treated with 0.1 ml of H₂O, and insoluble materials were removed by short-column (SiO₂, ether). Yields of the products were quantified by gas chromatography using *n*-docosane as an internal standard. Concentration of the mixture, followed by column chromatography (SiO₂, 6:1 *n*-hexane–ether) afforded 1-phenylcyclohexanol (**3**) (34 mg, 0.19 mmol) in 38% isolated yield as white crystals: m.p. 61.9–62.7°C (lit. [13] 62–63°C). IR (KBr) 3347.8 cm⁻¹; ¹H-NMR (CDCl₃): δ 1.29–1.33 (m, 1H), 1.61–1.90 (m, 10H), 7.21–7.25 (m, 1H), 7.31–7.37 (m, 2H), 7.49–7.52 (m, 2H); ¹³C-NMR (CDCl₃): δ 22.2, 25.5, 38.8, 73.1, 124.6, 126.7, 128.2, 149.4.

3.4. Reaction of diphenyliodonium trifluoromethanesulfonate (**1a**) with YbI₂ or SmI₂ and cyclohexanone

A solution of samarium iodide (0.1 M in THF, 5.0 ml) or ytterbium iodide (0.04 M in THF, 12.5 ml) was added into a Schlenk tube containing diphenyliodonium trifluoromethanesulfonate (**1a**) (53.9 mg, 0.125 mmol) and cyclohexanone (98.1 mg, 1.0 mmol) at room temperature. The resulting mixture was treated with 0.1 ml of H₂O, and insoluble materials were removed by short-column (SiO₂, ether). Yields of the products were quantified by gas chromatography using *n*-eicosane as an internal standard. A similar workup to Section 3.3 afforded 1-(oxacyclopent-2-yl)cyclohexanol (**4**) as colorless liquid. IR (neat) 3469.3, 1068.4 cm⁻¹; ¹H-NMR (CDCl₃): δ 1.21–1.93 (m, 15H), 3.68 (t, $J = 7.5$ Hz, 1H), 3.78–3.85 (m, 2H); ¹³C-NMR (CDCl₃): δ 21.5, 21.6, 25.2, 25.8, 26.2, 32.8, 35.8, 68.6, 71.7, 85.3. Anal. Calc. for C₁₀H₁₈O₂: C, 70.55; H, 10.66. Found: C, 70.77; H, 10.8%.

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