Samarium (II) Diiodide-Induced Reductive Cleavage of Se—Se and Te—Te Bond in Diphenyl Diselenide and Ditelluride Leading to a Samarium Phenylselenolate and Tellurolate: Preparation of Unsymmetrical Alkylphenyl Selenides and Tellurides

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ABSTRACT

Diphenyl diselenide and diphenyl ditelluride were reduced by samarium (II) diiodide in tetrahydrofuran-hexamethylphosphoric triamide to produce samarium phenylselenolate and samarium phenyltellurolate, respectively. This new selenolate or tellurolate anion species reacted smoothly with alkyl, allyl, and benzyl halides to give alkyl-, allyl-, and benzylphenyl selenides or tellurides in good yields under mild and neutral conditions. The samarium selenolate reacted with α-halo ketones to give the corresponding α-phenylseleno ketones. 1,4-Addition with α,β-enones proceeded to give 3-phenylseleno ketones in moderate yields. Isolation of phenylselenotributyltin or phenylseleno-trimethylsilane by transmetalation with tributyltin iodide or trimethylchlorosilane, respectively, suggested the presence of the samarium selenolate species.

Organoselenium and tellurium compounds have become markedly important not only as synthetic intermediates in organic synthesis but also as

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promising donor molecules for conductive materials [1]. A number of synthetic methods have been found to prepare organoselenium and tellurium derivatives. A convenient and general method to introduce a selenium or tellurium moiety into organic molecules is the reaction of a metal selenolate or tellurolate with appropriate electrophiles such as organic halides, epoxides, and α,β-enones. To prepare a metal organoselenolate, a symmetrical diselenide is often reduced by alkali metal (Li, Na) or hydride reducing agents [2–3]. Organoaluminum compounds are sometimes used to prepare aluminum selenolates [4–5]. Transmetalation of alkali metal organoselenolates with some organometallic halides, such as Me_3SiCl and Bu_3SnCl, leads to the corresponding metal selenolates ($Me_3SiSePh$ [6] and $Bu_3SnSePh$ [7]). Metal tellurolates [8] are prepared by similar methods, and their reactivites depend on the counter metallic species.

Samarium (II) diiodide (SmI_2) is a strong one-electron transfer reducing agent and much attention has recently been paid to its utilization in organic syntheses. We [9] and other workers [10] have reported some useful carbon–carbon bond formation induced by SmI_2. In our series of working with SmI_2 in organic syntheses, we have been interested in reductive cleavage of the Se—Se bond and the Te—Te bond in symmetrical diselenide and ditel-

luride by SmI_2. Most conventional reducing agents for symmetrical diselenides and ditellurides are strong bases, but SmI_2 is an efficient, mild, and neutral reducing agent. We now report the first preparations of samarium phenylselenolate and samarium phenyltellurolate that are good intermediates for the prepartion of unsymmetrical selenides and tellurides upon treatment with organic halides under mild and neutral conditions.

RESULTS AND DISCUSSION

We first examined whether the Se—Se bond in diphenyl diselenide would be cleaved by SmI_2 [11], inasmuch as the cleavage of the O—O bond in di-*tert*-butyl peroxide by SmI_2 has been reported to give samarium tert-butoxide as a trivalent samarium species [12]. Addition of diphenyl diselenide to a deep purple solution of SmI_2 in tetrahydrofuran (THF)-hexamethylphosphoric triamide (HMPA) resulted in a rapid change of color of the solution to dark brown, indicating that the Se—Se bond had been reductively cleaved by SmI_2 and that the trivalent samarium species had been formed. We assumed that this trivalent samarium species was the samarium phenylselenolate, $PhSeSmI_2$ (Scheme 1). On the other hand, the reductive cleavage reaction was very slow when HMPA was eliminated from the solvent mixture [13]; the THF solution was still blue green even after 10 h, showing the presence of unreacted divalent samarium [9–10]. The samarium phenylselenolate was never isolated but reacted smoothly with organic halides. Primary alkyl-, *sec*-alkyl-, allyl-, and benzylphenyl selenides formed easily in good yields (method A, see Experimental). The advantages of the reductive cleavage of di-

$$PhZPh + 2SmI_2 \xrightarrow[\text{THF-HMPA}]{} 2''PhZSmI_2'' \xrightarrow{RX} PhZR$$
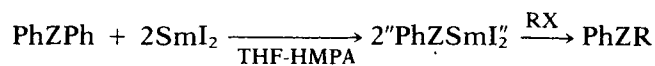
$$Z = Se, Te$$
$$X = Br, I$$

SCHEME 1

phenyl diselenide by SmI_2 are the mild and neutral conditions. The results are summarized in Table 1. The reaction can be carried out more conveniently by adding diphenyl diselenide and an organic halide simultaneously to SmI_2 (method B, see Experimental). However, this method seemed to be unsuitable for benzyl and allyl halides because reductive coupling of the organic halide always accompanied the simple nucleophilic substitution [14]. In this method, HMPA was again necessary to increase the reaction rate [13]; reaction of diphenyl diselenide and ethyl iodide was almost complete in 1 h in the presence of HMPA, but the conversion was only 20% in the absence of HMPA.

Similarly, the Te—Te bond in diphenyl ditelluride was cleaved immediately by SmI_2 in THF-HMPA and the resulting samarium phenyltellurolate reacted smoothly with alkyl halides to give alkylphenyl tellurides in good yields. These results are also shown in Table 1.

The phenylselenolate ion of the samarium salt successfully displaced the halogen moiety of an α-halo ketone, such as phenacyl chloride, to give the corresponding α-phenylseleno ketone (Scheme 2) (runs 8–9). However, the reaction of an α-halo ketone with selenolate anion has rarely been used to prepare an α-phenylseleno ketone [15]. Nucleophilic displacement on carbon is apparently accom-

TABLE 1 SmI_2 mediated Reaction of Diphenyl Diselenide or Ditelluride with Organic Halides[a]

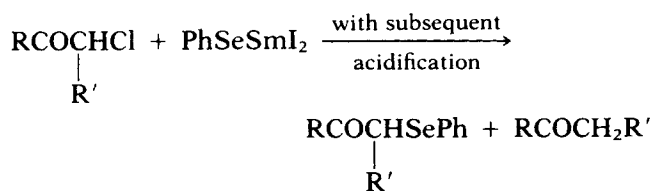| Run	Method[b]	PhZZPh	RX	Product	Yield (%)[c]
1	B	Z = Se	CH_3I	$PhSeCH_3$	58
2	B		CH_3CH_2I	$PhSeCH_2CH_3$	82
3	A		CH_3CH_2Br	$PhSeCH_2CH_3$	84
4	A		$(CH_3)_2CHBr$	$PhSeCH(CH_3)_2$	74
5	A		$PhCH_2Br$	$PhSeCH_2Ph$	69
6	A		$CH_2{=}CHCH_2I$	$PhSeCH_2CH{=}CH_2$	58
7	B		CH_2I_2	$PhSeCH_2SePh$	31
8	A		$PhCOCH_2Cl$	$PhSeCH_2COPh$	58[d]
9	A		$CH_3COCH(CH_3)Cl$	$PhSeCH(CH_3)COCH_3$	75
10	B	Z = Te	CH_3I	$PhTeCH_3$	70
11	B		CH_3CH_2I	$PhTeCH_2CH_3$	81
12	B		$CH_3CH_2CH_2I$	$PhTeCH_2CH_2CH_3$	82
13	A		$PhCH_2Br$	$PhTeCH_2Ph$	68
14	A		$PhCOCH_2Cl$	—[e]	0

[a] PhZZPh, 0.5 mmol; RX, 1 mmol; SmI_2, 1.2 mmol; THF-HMPA (20:1); room temperature, 1 h.
[b] See Experimental.
[c] Isolated yield based on PhZZPh.
[d] Acetophenone, 25%.
[e] Acetophenone was produced almost quantitatively.

RCOCHCl + PhSeSmI$_2$ $\xrightarrow[\text{acidification}]{\text{with subsequent}}$
|
R'

RCOCHSePh + RCOCH$_2$R'
|
R'

SCHEME 2

panied by nucleophilic displacement on halogen to produce, on subsequent protonation, the parent ketone [16]. The phenyltellurolate anion apparently effected only a simple displacement on halogen in the reaction with phenacyl chloride (run 14); acetophenone was produced, but no α-phenyltelluro ketones [17].

With α,β-enones, such as methyl vinyl ketone and 2-cyclohexenone, 1,4-addition proceeded to give the corresponding 3-phenylseleno ketones in 18% and 35% yields, respectively (Scheme 3) [18].

To confirm the formation of the samarium selenolate as an intermediate, we performed transmetalation reactions, with trimethylchlorosilane and tributyltin iodide respectively (Scheme 4). Phenylseleonotrimethysilane [6] and phenylselenotributyltin [7], respectively, were isolated quantitatively by these reactions, indicating the formation of the samarium selenolate species as an intermediate.

EXPRIMENTAL

General

^{1}H NMR spectra were recorded with a Hitachi R-24 (60 MHz) instrument, with carbon tetrachloride used as the solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined on a Fourier transform NMR system (JEOL JNM EX-90) with CDCl$_3$ as solvent. GLC analyses were carried out using a Shimadzu 8A apparatus on EGSS-X(3%)-Chromosorb-W(2 m) and Silicone DC QF-1(5%)-Chromosorb-W(2 m) columns (N$_2$ as carrier gas). Preparative TLC separation was conducted using 20 × 20 cm glass plates coated with a 2.0 mm thick layer of Merck Kieselgel PF$_{254}$ gipsphaltig.

Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Commercial

SCHEME 3

PhSeSmI$_2$ + Me$_2$SiCl $\longrightarrow$ PhSeSiMe$_3$
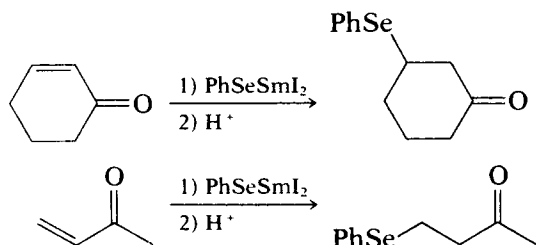
PhSeSmI$_2$ + Bu$_3$SnI $\longrightarrow$ PhSeSnBu$_3$
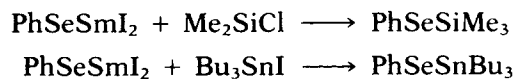
SCHEME 4

HMPA was dried over calcium hydride, distilled in vacuo, and stored over 4 Å molecular sieves. All organic halides are commercially available and were used without further purification unless otherwise noted. Samarium (99.9% purity) was provided by the Shin-Etsu Chemical Co. Ltd and Nippon Rare Earth Co. Ltd. Diphenyl diselenide [19] and diphenyl ditelluride [20] were prepared by the reaction of phenylmagnesium bromide with selenium (Nacalai Chemicals Co. Ltd.) and tellurium (Aldrich Chemical Co. Ltd.) powders, respectively.

Reaction of Diphenyl Diselenide or Ditelluride with Organic Halides Mediated by SmI$_2$

The following are general procedures for the preparation of alkyl phenyl selenides or tellurides using SmI$_2$.

Method A (two step method). Samarium powder (0.20 g, 1.3 mmol) [21] was placed in a well-dried two neck round bottom flask containing a magnetic stirrer bar. The flask was flushed with nitrogen several times. Methylene diiodide (0.32 g, 1.2 mmol) in THF (7 mL) was added through a rubber septum by a syringe. The mixture was stirred at room temperature until the solution became deep green and homogeneous (0.5–1 h). HMPA (0.7 mL) was then added and the solution became deep purple; the THF-HMPA solution of SmI$_2$ was ready for subsequent use. To the THF-HMPA solution of SmI$_2$ was added diphenyl diselenide (0.17 g, 0.5 mmol) or ditelluride (0.21 g, 0.5 mmol) in one portion at room temperature under nitrogen; the deep purple color of the solution disappeared immediately and the solution became dark brown. The resulting solution was stirred at room temperature for 1 h. The organic halide (1 mmol) was then added to the solution and the mixture was stirred for 3 h. Then the whole solution was poured into dil HCl, and the mixture was extracted with ether (15 mL × 2). The ethereal solution was treated with aq Na$_2$S$_2$O$_3$, washed with brine, and dried over MgSO$_4$. Evaporation of the solvent left a yellow oil that was subjected to preparative TLC on silica gel (petroleum ether as eluent). GLC analysis revealed the presence of the corresponding alkylphenyl selenide or telluride. The product was isolated by preparative TLC on silica gel.

Method B (one step method). To the THF-HMPA (7 mL-0.7 mL) solution of SmI$_2$ (1.2 mmol), prepared as described above, was added a mixture of dipheny diselenide (0.17 g, 0.5 mmol) or ditelluride

(0.21g, 0.5 mmol) and organic halide (1 mmol) in THF (7 mL) at room temperature, and the solution was stirred for 5 h, during which time its color changed into brownish yellow. The reaction solution was poured into dil HCl, and the mixture was extracted with ether (15 mL × 2). The ethereal solution was treated with aq $Na_2S_2O_3$, washed with brine, and dried ($MgSO_4$). Evaporation of the solvent left a yellow oil that was subjected to preparative TLC on silica gel (petroleum ether as eluent). The phenylalkyl selenides [2, 3, 6a] and tellurides [22] prepared have been reported.

α-Phenylselenoacetophenone [15c]. Yellow oil; R_f = 0.70 (silica gel, hexane:diethyl ether = 1:1); ^1H NMR (CCl_4) δ 3.89 (s, 3H), 7.0–7.5 (m, 8H), 7.5–7.8 (m, 2H).

3-Phenylseleno-2-butanone [15a]. Yellow oil; R_f = 0.75 (silica gel, hexane:diethyl ether = 1:1); ^1H NMR (CCl_4) δ 1.31 (d, 3H, J = 7.0 Hz), 2.09 (s, 3H), 3.60 (q, 1H, J = 7.0 Hz), 7.0–7.6 (m, 5H).

Reaction of Diphenyl Diselenide with α,β-Unsaturated Ketones Mediated by SmI_2

A typical experimental procedure is as follows. To the THF-HMPA (5 mL-0.5 mL) solution of SmI_2 (1.2 mmol) was added diphenyl diselenide (0.17 g, 0.5 mmol) in one portion at room temperature under nitrogen; the deep purple color of the solution disappeared immediately and the solution became yellow brown. The resulting solution was stirred at room temperature for 1 h. 2-Cyclohexen-1-one (1 mmol) was then added to the solution and the mixture was stirred for 5 h. The reaction was monitored by TLC analysis of the reaction mixture, which suggests the presence of two organoselenium compounds including diphenyl diselenide. After the usual workup, the product was isolated by preparative TLC on silica gel (hexane-ether as eluent).

3-Phenylselenocyclohexanone [18a]. Pale yellow oil; R_f = 0.65 (silica gel, hexane:ether = 1:1); ^1H NMR (CCl_4) δ 0.8–1.8 (m, 8H), 2.0–2.3 (m, 1H), 6.9–7.6 (m, 5H). ^{13}C NMR δ 26.5 (t), 33.4 (t), 41.6 (t), 42.2(t), 50.0 (d, PhSeCH), 129.5 (d), 130.4 (d), 132.8 (d), 137.0 (d), 151.9 (s), 210.0 (s, C=O).

4-Phenylseleno-2-butanone [6a, 18a]. Pale yellow oil; R_f = 0.55 (silica gel, hexane:ether = 1:1); ^1H NMR (CCl_4) δ 2.05 (s, 3H), 2.6–3.1 (m, 4H), 7.1–7.6 (m, 5H).

Transmetalation Reaction of Diphenyl Diselenide with Trimethylchlorosilane Mediated by SmI_2

To the dark brown THF-HMPA (5 mL-0.5 mL) solution prepared from SmI_2 (1.2 mmol) and diphenyl

diselenide (0.17 g, 0.5 mmol) as described above, was added trimethylchlorosilane by injection through a rubber septum by a syringe at room temperature. The mild exothermic reaction occurred instantaneously. After 1 h stirring at an ambient temperature, the solution was diluted with dry hexane (50 mL) and the precipitate was removed by filtration. The precipitate was further washed with dry hexane (20 mL) and the filtrates were combined. The solvent was removed by a rotary evaporator under vacuum. A ^1H NMR spectral measurement of the residue indicates the formation of almost pure phenylselenotrimethylsilane [6]. Yield, 227 mg, 0.99 mmol, 99%.

Phenylselenotributyltin was prepared by using tributyltin iodide by the same procedure as applied to phenylselenotrimethylsilane except for the workup procedures. The reaction solution was diluted with hexane (50 mL) and the precipitate was removed by filtration. The hexane solution was treated with aq potassium fluoride solution to precipitate the unreacted starting tributyltin iodide as insoluble tributyltin fluoride. The organic layer was dried over $MgSO_4$ and the solvent was removed by evaporation. Separation by short column chromatography (3 × 5 cm) of the residue gave almost pure phenylselenotributyltin as a yellow oil [7]. Yield, 440 mg, 0.99 mmol, 99%.

ACKNOWLEDGMENT

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