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A New Method for the Synthesis of Organotellurium Compounds by the Use of Reductive Cleavage of the Tellurium–Tellurium Bond with Lanthanum Metal

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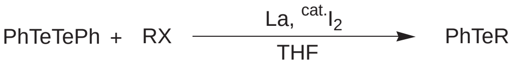
It was confirmed that lanthanum metal is an efficient reagent for the reductive cleavage of the tellurium–tellurium bond of ditelluride. Alkyl phenyl tellurides were prepared by the reaction of diphenyl ditelluride with primary and secondary alkyl halides in the presence of lanthanum metal and a catalytic amount of iodine in moderate to good yields. The reaction was accelerated by the addition of HMPA. In addition, the reduction of ditelluride with lanthanum metal, followed by the addition of acyl or aroyl chlorides or α,β-unsaturated ester, provided the *Te*-phenyl tellurol esters and the β-phenyl telluro ester in moderate yields.

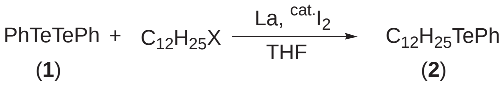
There is increasing interest in the chemistry of organotellurium compounds, and much effort is being devoted to accomplish the synthesis of organotellurium compounds.[1] Although there have been numerous reports on the synthesis of organotellurium compounds, it usually requires the handling of reagents that are unstable in air and moisture, under strongly basic or acidic reaction conditions, and involving the use of multi-step procedures for the preparation of the tellurium reagents.[1a,1d,2] Thus, the development of a one-step synthetic procedure using a stable tellurium reagent under neutral conditions has attracted much attention. In this paper, we report on a new approach for the synthesis of organotellurium compounds by using reductive cleavage of the tellurium–tellurium bond of ditelluride with lanthanum metal (Scheme 1).[3]



$$\mathrm{PhTeTePh} + \mathrm{RX} \xrightarrow[\mathrm{THF}]{\mathrm{La,\ ^{cat.}I_2}} \mathrm{PhTeR}$$

Scheme 1.

Table 1. Reaction of PhTeTePh with Halododecane[a)]

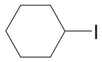
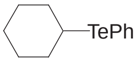
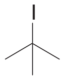
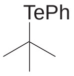


$$\underset{(\mathbf{1})}{\mathrm{PhTeTePh}} + \mathrm{C_{12}H_{25}X} \xrightarrow[\mathrm{THF}]{\mathrm{La,\ ^{cat.}I_2}} \underset{(\mathbf{2})}{\mathrm{C_{12}H_{25}TePh}}$$

Entry	RX	Temp./°C	Yeild/%[b)]
1	$C_{12}H_{25}I$	25	90
2	$C_{12}H_{25}Br$	67	89
3		25	37
4[c)]		25	87
5	$C_{12}H_{25}Cl$	25	trace
6		67	49
7[c)]		25	90

a) Reaction conditions: PhTePh (1.0 mmol), $C_{12}H_{25}X$ (2.0 mmol), La (1.0 mmol), I_2 (0.2 mmol), and THF (3.0 mL) for 5 h. b) GC yield based on $C_{12}H_{25}X$. c) HMPA (1.0 mL) was added.

Table 2. Synthesis of Alkyl Phenyl Telluride[a)]

Entry	RX	Temp./°C	Product	Yield/%[b)]
1	C_4H_9I	25	C_4H_9TePh (**3**)	92
2	$C_6H_{13}I$	25	$C_6H_{13}TePh$ (**4**)	91
3	$(CH_3)_2CHI$	67	$(CH_3)_2CHTePh$ (**5**)	54
4[c)]		25	(**5**)	93
5	$C_2H_5CH(CH_3)I$	67	$C_2H_5CH(CH_3)TePh$ (**6**)	65
6[c)]		25	(**6**)	100
7		67	 (**7**)	11
8[c)]		25	(**7**)	67
9		67		0

a) Reaction conditions: PhTeTePh (1.0 mmol), RI (2.0 mmol), La (1.0 mmol), I_2 (0.2 mmol), and THF (3.0 mL) for 5 h. b) GC yield based on RX. c) HMPA (1.0 mL) was added.

When diphenyl ditelluride (**1**) (1.0 mmol) was allowed to react with two equivalent amounts of 1-iodododecane (2.0 mmol) in the presence of lanthanum metal (1.0 mmol) and a catalytic amount of iodine (0.2 mmol) in THF (5 mL) as a solvent at 25 °C for 5 h, 1.80 mmol of dodecyl phenyl telluride (**2**) was obtained (90% yield based on 1-iodododecane) (Table 1, entry 1).[9] Two phenyltelluro groups contained in **1** were efficiently utilized in the reaction. The reaction of chloro- and bromododecane was successfully carried out by elevating the reaction temperature to produce **2** in 49 and 89% yields, respectively (entries 2 and 6). It is of interest to note that the reaction was accelerated by the addition of HMPA, and **2** was obtained in good yield, even when the reaction was carried out at 25 °C (entries 4 and 7).[10]

The results of the reaction of diphenyl ditelluride (**1**) with various alkyl halides in the presence of lanthanum metal are given in Table 2. When **1** was allowed to react with primary alkyl iodides under the same reaction conditions as entry 1 in Table 1, the yields of the primary alkyl phenyl telluride were high (entries 1 and 2). For the secondary alkyl iodide, such as 2-iodopropane and 2-iodobutane, the yields of the telluride were slightly lower under similar reaction conditions to that of the primary alkyl iodides; however, the yields were improved by the addition of HMPA (entries 4 and 6). Cyclohexyl phenyl telluride was also obtained in 67% yield (entry 8). In

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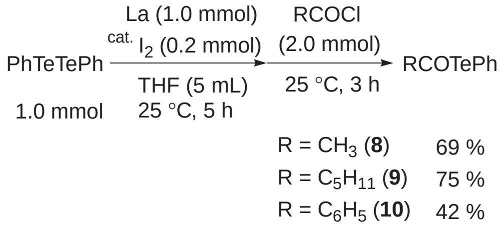
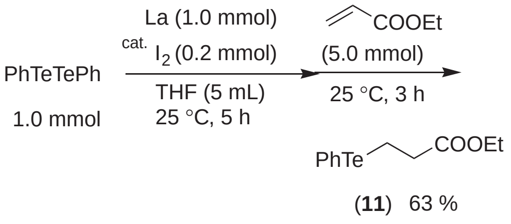
the reaction of tertiary alkyl iodide, no alkyl phenyl telluride was formed, and the alkyl halide was recovered (entry 9). The reaction of benzyl bromide resulted in the formation of benzaldehyde in 62% yield.[11]

Although the syntheses of the *Te*-phenyl tellurol esters by the lanthanum metal-assisted reaction of diphenyl ditelluride (**1**) with acyl or aroyl chlorides were next carried out, the yields of *Te*-phenyl tellurol esters were low, due to the formation of various by-products. The product yields were improved by using a two-step procedure. Diphenyl ditelluride (**1**) was allowed to react with lanthanum metal in the presence of a catalytic amount of iodine at 25 °C for 5 h, and then the acyl or aroyl chloride was added to the resulting solution, producing *Te*-phenyl tellurol esters in 42–75% yields (Scheme 2). Similarly, a reaction of the α,β-unsaturated ester efficiently occurred to afford the β-phenyltelluro ester in 63% yield (Scheme 3). In the case of epoxide, such as 1,2-epoxybutane, the yield of 2-hydroxy-1-phenyltellurobutane was very low (7%) owing the preparation of various by-products.

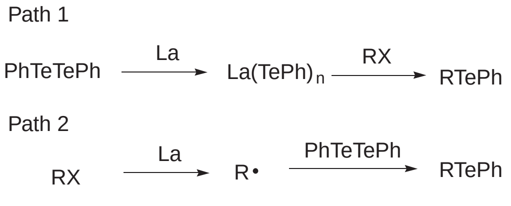
Nakamura and Mashima et al. have shown a direct synthetic method toward lanthanoid thiolate complexes (La = Sm and Eu) via the reaction of diaryl disulfide with samarium or europium metal in the presence of a catalytic amount of iodine.[12] We have recently found that alkyl radicals were easily generated by the reduction of alkyl halides with lanthanum metal, which coupled to form the corresponding dimerization products.[13] Based on these bachgrounds, two reaction pathways for the formation of organotellurium compounds are shown in Scheme 4.[14] One is the reaction of lanthanum phenyltellurolate, prepared by the reduction of ditelluride with lanthanum metal with alkyl halides (Path 1). Another pathway including the S_H2 reaction of alkyl radicals, which was generated by the reduction of alkyl halides with lanthanum metal, with ditelluride was suggested (Path 2). To better understand the reaction pathway, we carried out some experiments, and obtained the following results. When PhTeTePh was treated with lanthanum metal, lanthanum metal was gradually dissolved to give a brown solution. Subsequently, the addition of 1-iodododecane to the solution provided dodecyl phenyl telluride in 87% yield. On the other hand, when 1-chlorododecane was added to the brown solution, no alkyl phenyl telluride was formed. Furtheremore, the addition of HMPA to the resulting solution caused the formation of dodecyl phanyl telluride (67%). Based on these results, at the present time, while the preparation pathway of organotellurium compounds was not clearly shown, the reaction pathway including the alkylation of lanthanum phenyltellurolate with alkyl halides was strongly suggested.



Scheme 2.



Scheme 3.



Scheme 4.

We found a new method for synthesizing alkyl phenyl tellurides by the reaction of diphenyl ditelluride with alkyl halides in the presence of lanthanum metal. *Te*-Phenyl tellurol esters or β-phenyltelluro ester were synthesized by the reduction of ditelluride with lanthanum metal, followed by the addition of acid chloride or α,β-unsaturated esters.

Experimental

General Procedures. The ^{1}H and ^{13}C NMR spectra were recorded on 400 and 99.5 MHz spectrometers using $CDCl_3$ as the solvent with tetramethylsilane as the internal standard. The IR spectra were recorded on a FT-IR spectrophotometer. Gas chromatography (GC) was carried out using a flame-ionizing detector-equipped instrument and a capillary column (0.25 mm × 25 m). HPLC separation was performed using recycling preparative HPLC equipped with GPC columns (20 mm × 1200 mm).

Reagents. The organic halides and iodine were commercially available high-grade products, and were used without purification. The lanthanum metal was a commercially available high-grade product, which was used after powderization with a rasp. The metal was stocked under a nitrogen atmosphere. Diphenyl ditelluride was synthesized as described in the literature.[15] The other reagents and solvents were purified before use by the usual methods.

General Procedure for the Reaction of Diphenyl Ditelluride with Organic Halides in the Presence of Lanthanum Metal. Lanthanum powder (1.0 mmol, 139 mg), iodine (0.2 mmol, 51 mg) and diphenyl ditelluride (1.0 mmol, 409 mg) were placed in a two-necked flask. THF (5 mL) and the organic halide (2.0 mmol) were added to the flask, and the mixture was stirred at 25 or 67 °C for 5 h under a nitrogen atmosphere. After the reaction, aqueous HCl (1 M) was added to the reaction mixture, and the mixture was extracted with diisopropyl ether. The organic layer was dried over $MgSO_4$ and filtered. The organic solvent was removed under reduced pressure. Purification of the residue by HPLC afforded the corresponding alkyl phenyl telluride. The products were characterized by a comparison of their spectra data with those of authentic samples (**2**,[9] **3**,[16] **4**,[17] **5**,[17] **6**,[17] and **7**[18]).

General Procedure for the Synthesis of Alkyl Phenyl Telluride in the Presence of HMPA. Lanthanum powder (1.0 mmol, 139 mg), iodine (0.2 mmol, 51 mg), PhTeTePh (1.0 mmol, 409 mg), RI (2.0 mmol), HMPA (1 mL) and THF (5 mL) were added to the flask, and the mixture was stirred at 25 °C for 5 h under a nitrogen atmosphere. After the reaction, the same workup as described in general procedure for the reaction of diphenyl ditelluride with organic halide was carried out to give the corresponding alkyl phenyl tellurides.

Two Step Procedures for Synthesis of Organotellurium Compounds. A THF (5 mL) solution of lanthanum powder (1.0 mmol, 139 mg), iodine (0.2 mmol, 51 mg) and PhTeTePh (1.0 mmol, 409 mg) was stirred at 25 °C for 5 h under a nitrogen atmosphere. The acyl or aroyl chlorides or α,β-unsaturated ester (2.0 mmol) was added to the resulting solution, and the mixture was stirred at 25 °C for 3 h. After the reaction, the same workup as described in the general procedure for the reaction of diphenyl ditelluride with organic halide, was carried out to give the corresponding organotellurium compound. The product was characterized by comparing its spectra data with those of authentic samples (**8**,[19] **10**,[20] and **11**[21]). The structures of the product (**9**) were assigned by their ^{1}H and ^{13}C NMR and IR spectra.

***Te*-Hexyl Tellurobenzoate (9):** ^{1}H NMR ($CDCl_3$) δ 0.86–1.00 (m, 3H, CH_3), 1.25–1.34 (m, 4H, CH_2), 1.60–1.68 (m, 2H, CH_2), 2.67 (t, $J = 7.6$ Hz, 2H, CH_2), 7.25–7.76 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.2, 14.5, 22.3, 24.6, 54.9, 114.0, 128.8, 130.3, 139.3, 140.8, 202.9; IR (neat) 3054.8, 2929.3, 1719.0, 1572.2, 1474.3, 1434.7, 1115.7, 997.7, 731.3, 690.0 cm^{-1}.

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