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A new, practical synthesis of organotellurium compounds from organic halides and silyl tellurides. Remarkable effects of polar solvents and leaving groups

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Abstract—Silyl tellurides react with organic halides to give the corresponding organotellurium compounds and silyl halides in good to excellent yields. Substitution proceeds in polar solvents, such as acetonitrile, but not in nonpolar solvents under identical conditions. The leaving group also plays a significant role, with alkyl bromides being the most reactive, alkyl chlorides less so and alkyl iodides the least reactive. After removal of the volatile silyl halides and solvent under vacuum, the essentially pure organotellurium compounds, which can be used directly as precursors for carbocations, carbanions, and carbon-centered radicals, were obtained. © 2001 Elsevier Science Ltd. All rights reserved.

Divalent organotellurium compounds have attracted a great deal of attention[1] because of their synthetic utility. Since they serve as excellent precursors of carbanions by transmetallation,[2] of carbocations by oxidation,[3,4] and of carbon-centered radicals by reaction with radical mediators or by photolysis and thermolysis,[5,6] a number of methods for their preparation have been developed. Most of these syntheses rely on nucleophilic substitution of lithium or sodium tellurolates with appropriate electrophiles, such as organic halides and sulfonates.[1a,7] Various new metal tellurates, e.g. stannyl tellurides[8] and samarium tellurides,[9] have been recently employed to increase efficiency and selectivity. Homolytic substitution of ditellurides with carbon-centered radicals,[10] and condensation of alcohols with telluro-cyanates have also been developed.[11] However, the problem with the synthesis of organotellurium compounds is often not the reaction but the isolation and purification of the products. In many cases, certain organotellurium compounds are unstable under air or routine purification conditions, such as silica gel chromatography. As a result, organotellurium compounds are often used in the following step without purification. Therefore, it would be highly desirable to develop an efficient and practical synthetic route, which requires no troublesome workup and/or purification.

We have recently reported that silyl tellurides show unique reactivity toward carbonyl compounds and quinones, especially in polar solvents.[12] During our investigation of silyl tellurides, we found that they react with organic halides in polar solvents without catalysts.[13] We report here a new and practical synthesis of organotellurium compounds by the thermal substitution reaction of trimethylsilyl phenyl telluride (**1**) and organic halides (Eq. (1)).[14] The reaction proceeds under neutral conditions and affords the corresponding organotellurium compounds in good to excellent yields. Since the trimethylsilyl halide generated was easily removed under reduced pressure, we obtained the essentially pure organotellurium compounds, which could be used directly for further synthetic transformations.

$$\underset{\mathbf{1}}{\mathrm{Me_3SiTePh}} + \mathrm{RX} \xrightarrow[\mathrm{MeCN}]{} \mathrm{RTePh} + \mathrm{Me_3SiX} \qquad (1)$$

We first examined the reaction of 1-decyl bromide (66.4 mg, 0.30 mmol) and **1** (83.4 mg, 0.30 mmol) in acetonitrile (1.0 mL) at 60°C for 12 h, and found that the reaction proceeded smoothly to give 1-decyl phenyltelluride in quantitative yield, as judged by ^{1}H NMR (Table 1, entry 1). The reaction also produced trimethylsilyl bromide, which was characterized by ^{1}H NMR in the experiments carried out in CD_3CN. The progress of the reaction was found to be strongly

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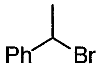
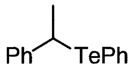
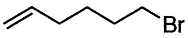
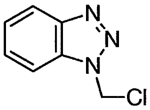
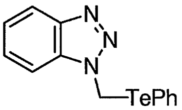
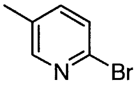
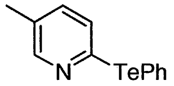
influenced by the polarity of the solvent. Thus, the reaction took place efficiently in polar solvents, e.g. acetonitrile, DMF, pyridine, and the ionic liquid (1-butyl-3-methyl-1-imidazolium tetrafluoroborate),[15] while no reaction occurred in non-polar solvents, e.g. THF and toluene, under similar conditions. Acetonitrile was selected as the solvent for the following investigation because of its volatility.

We next examined the effect of leaving groups and found that, surprisingly, alkyl bromides were most reactive, alkyl chlorides less so and alkyl iodides the least reactive. Thus, even though the reaction of 1-decyl chloride had not gone to completion after 24 h at 60°C, the desired product formed in 87% yield (entry 2). Conversely, only half the amount of 1-decyl iodide was converted to the product under similar conditions (entry 3).[16]

The present reaction was applied to a variety of benzyl, allyl, and alkyl halides; its scope and efficiency are summarized in Table 1. Benzyl halides are especially good substrates, and both bromides and chlorides reacted to give the corresponding tellurides in quantitative yields (entries 4–7). Substitution took place exclusively at the *sp*^{3} carbon–chlorine bond over the *sp*^{2} carbon–chlorine bond (entries 5 and 6). The secondary benzyl bromide also afforded the desired product in good yield (entry 7), while allyl halides, equally good substrates, furnished the desired products in excellent yields (entries 8 and 9). It is worth noting that unstable benzylic and allylic tellurides could be easily characterized by ^{1}H and ^{13}C NMR after removal of trimethylsilyl bromide and solvent under vacuum, followed by the introduction of deuterated solvents. Primary alkyl bromides are also quite reactive (entries 1, 10 and 11).

Table 1. Synthesis of organotellurium compounds from organic halides and silyl telluride **1**[a]

Entry	RX	Solvent	Temp. (°C)	Time (h)	Product	Yield %[b]
1	*n*-$C_{10}H_{21}Br$	Acetonitrile	60	12	*n*-$C_{10}H_{21}TePh$	100 (84)[c]
		Pyridine	60	3		88
		DMF	60	3		63
		Ionic liquid[d]	60	3		37
		THF	60	3		0
		Toluene	60	3		0
2	*n*-$C_{10}H_{21}Cl$	Acetonitrile	60	24	*n*-$C_{10}H_{21}TePh$	87 (57)[c]
3	*n*-$C_{10}H_{21}I$	Acetonitrile	60	24	*n*-$C_{10}H_{21}TePh$	41 (23)[c]
4	$PhCH_2Br$	Acetonitrile	r.t.	1	$PhCH_2TePh$ (**2**)	100[e]
5	*o*-$ClC_6H_4CH_2Cl$	Acetonitrile	r.t.	0.5	*o*-$ClC_6H_4CH_2TePh$	100
6	*m*-$ClC_6H_4CH_2Cl$	Acetonitrile	r.t.	0.5	*m*-$ClC_6H_4CH_2TePh$	100
7		Acetonitrile	60	6		72
8	$H_2C=CHCH_2Br$	Acetonitrile	r.t.	1.5	$H_2C=CHCH_2TePh$	98[e]
9	*trans*-$PhCH=CHCH_2Cl$	Acetonitrile	r.t.	3.5	*trans*-$PhCH=CHCH_2TePh$	90
10		Acetonitrile	60	4		91
11		Acetonitrile	r.t.	1.5		95[f]
12	*c*-$C_6H_{11}Br$	Acetonitrile	100	24	*c*-$C_6H_{11}Br$	60
13	*t*-BuBr	Acetonitrile	60	24	*t*-BuTePh	36
14		Acetonitrile	60	48		48

[a] Typical experimental procedures: A mixture of alkyl halide and **1** (1.0 – 1.1 equiv) in acetonitrile (ca. 0.5 M solution) was stirred at the temperature indicated in the Table. After removal of the volatile materials under vacuum, the product was analyzed by ^{1}H and ^{13}C NMR. [b] As the products formed were unstable under the conditions of silica gel chromatography, the yields were determined by ^{1}H NMR of the crude mixture after adding an internal standard. [c] Yield corresponding to the reaction at 60 °C for 3 h. [d] 1-Butyl-3-methyl-1-imidazolium tetrafluoroborate was used. [e] Corresponding chlorides also gave the same product in quantitative yield after stirring at r.t. for 3 h. [f] Slight excess of **1** (1.5 equiv) was used.

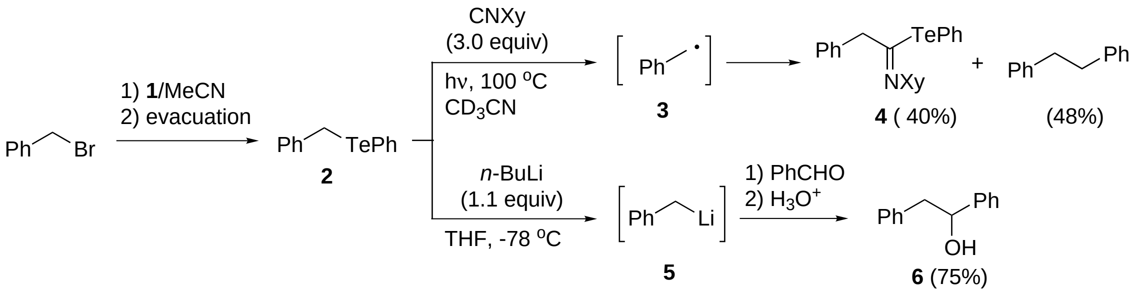


Figure 1. One-pot generation of benzyl radical and anion from benzyl bromide.

α-Amino tellurides, which are excellent precursors for α-amino radicals,[6f] could be easily prepared from the corresponding chlorides (entry 11). Secondary alkyl bromides were found to be moderately reactive (entry 12), while tertiary alkyl bromides were unreactive (entry 13). Aryl halides, such as bromo- and iodobenzene, did not react under similar conditions, whereas 2-pyridyl bromide reacted to give the corresponding telluride in moderate yield (entry 14). This is probably because the strong directing effect of the 2-pyridinyl group enhances the reactivity.[17]

A synthetic advantage of the current method is the ease of workup. Because the side products formed are the volatile trimethylsilyl halides, the essentially pure products could be easily obtained after removal of the silyl halide and the solvent under vacuum. The crude product could then be used for further synthetic transformations. For example, benzyl phenyl telluride (**2**), which was obtained in essentially pure form by the reaction of benzyl bromide and **1** followed by evacuation, was used directly as a precursor of the benzyl radical and anion species (Fig. 1). Thus, the crude **2** was heated with 2,6-dimethylphenyl isonitrile (CNXy) under irradiation to obtain the imidoylated product **4** and 1,2-diphenylethane by way of the benzyl radical **3**.[6f] Furthermore, treatment of the crude **2** with one equiv. of *n*-BuLi selectively cleaved the benzylic C–Te bond to generate the benzyl lithium **5**,[18] which added to benzaldehyde to give **6** in good yield.

A detailed mechanism of the current reaction is unclear at the present time. The fact that 1-hexenyl 6-bromide did not give the cyclized product (entry 10) suggests that a mechanism involving free radical-mediated substitution is unlikely.[12,19] Instead, the observed solvent effect is coincidental with the involvement of a polar transition state or intermediate, which is stabilized in polar solvents. Further synthetic investigations, as well as mechanistic studies are underway.

Typical experimental procedure for the one-pot generation of benzyllithium via benzyl phenyl telluride. A solution of benzyl bromide (51.3 mg, 0.30 mmol) and **1** (83.4 mg, 0.30 mmol) in acetonitrile (1.0 mL) was stirred at room temperature for 1 h. After the volatile materials were evacuated under reduced pressure, the crude benzyl phenyl telluride (**2**) was obtained in almost pure form, as judged by ^{1}H NMR. THF (1.0 mL) was introduced to the crude **2**, and to the resulting solution was added BuLi in hexane (1.53 M solution, 0.22 mL, 0.33 mmol) at −78°C. The resulting mixture was stirred for 15 min at this temperature, and benzaldehyde (33.5 μL, 0.33 mmol) was added. After being stirred for 30 min at −78°C, the reaction mixture was quenched by addition of methanol (1.0 mL). After the usual workup, purification by silica gel chromatography afforded **8** in 75% yield (44.5 mg, 0.23 mmol).

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