Phenyltellanyl Triflate (PhTeOTf) as a Powerful Tellurophilic Activator in the Friedel–Crafts Reaction

Takeshi Yamada,[1] Eri Mishima,[2] Kazuya Ueki,[2] and Shigeru Yamago*[2]
[1]*Pioneering Research Unit for Next Generation, Kyoto University, Kyoto 611-0011*
[2]*Institute for Chemical Research, Kyoto University, Kyoto 611-0011*

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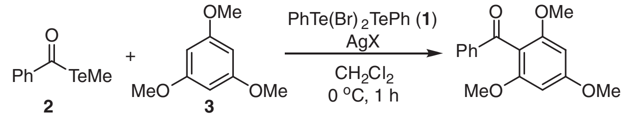
A powerful electrophilic activator for organotellurium compounds was developed. Phenyltellanyl triflate (PhTeOTf) prepared in situ from dibromophenyl(phenyltellanyl)telluride and AgOTf selectively activated various organotellurium compounds in the presence of aromatic compounds yielding the corresponding Friedel–Crafts reaction products. Polymer-end organotellurium compounds were also activated by PhTeOTf providing the corresponding end-functionalized polymers.

Organoheteroatom compounds have been widely used as the precursors for reactive carbon species, such as carbanions, carbocations, and carbon-centered radicals, which are essential intermediates in organic synthesis. Among these, organotellurium compounds have been recognized as some of the most versatile precursors due to their simple preparation methods, considerable stabilities, and high reactivities.[1] For example, various organometallic reagents are prepared from organotellurium compounds by the tellurium–metal exchange reaction.[2] Carbon-centered radicals generated from organotellurium compounds are also used for the controlled synthesis of small molecules[3] and macromolecules.[4] We recently showed that a dual use of organotellurium compounds as the precursors of both carbon-centered radicals and carbanions offered unique synthetic transformations, which were unattainable with a single carbon-reactive species.[5] By contrast, the generation of carbocations from organotellurium compounds has been limited,[6] especially in applications with carbon–carbon bond-formation reactions.[7] These results prompted us to investigate the use of organotellurium compounds as the precursors of carbocationic species. We hypothesized that this situation could be attributed to the lack of a suitable activator of organotellurium compounds, and that the development of an efficient activator would open new possibilities for their use in electrophilic reactions. Here, we report on a new and efficient tellurophilic activator, and its utilization in the Friedel–Crafts reaction.

We focused on dibromophenyl(phenyltellanyl)telluride (**1**)[8] as a precursor of an electrophilic activator. A recent study indicated that **1** reversibly generated PhTeBr at ambient temperature. Thus, **1** prepared by mixing an equimolar amount of diphenylditelluride and bromine was treated with 2 equiv of AgOTf at 0 °C in CH_2Cl_2 for 0.5 h, and a mixture of acyl telluride **2** and 1,3,5-trimethoxybenzene (**3**) was added to this solution at 0 °C. After aqueous workup, the Friedel–Crafts product was identified in 66% yield by ^1H NMR analysis (Table 1, Entry 1). The yield increased to 91% when the acylation was carried out at room temperature (Entry 2). As neither **1** nor AgOTf activated **2** under similar conditions (<6% yield), PhTeOTf generated from these reagents must be the real activating species (see below). The synthetic advantages of acyl tellurides are also worth mentioning, because they are more hydrolytically stable and easier to purify than acyl halides, which are routinely used as substrates in the Friedel–Crafts reaction.

Table 1. Friedel–Crafts acylation of acyltelluride **2** and 1,3,5-trimethoxybenzene (**3**) with a tellurophilic activator[a]



Entry	Activator	Yield/%[b]
1	**1**/AgOTf	66
2[c]	**1**/AgOTf	91
3	**1**/$AgNTf_2$	53
4	**1**/$AgSbF_6$	49
5	**1**/$AgB(C_6F_5)_4$	24
6	PhSeOTf	50
7	PhSOTf	44

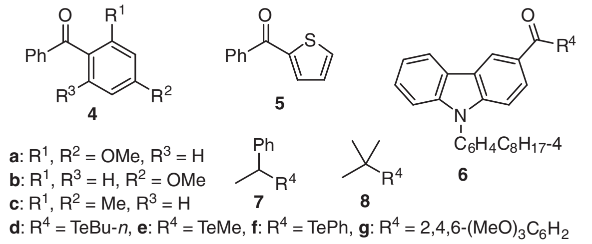
[a]The activator prepared from **1** (0.15 mmol) and AgOTf (0.41 mmol) was added to a CH_2Cl_2 solution of **2** (0.26 mmol) and **3** (0.29 mmol) at 0 °C. [b]Determined by ^1H NMR based on **2**. [c]The reaction was carried out at room temperature.

Activators in situ prepared from **1** and $AgNTf_2$, $AgSbF_6$, and $AgB(C_6F_5)_4$ also served as the activators (Entries 3–5), but their efficiency was lower than that of PhTeOTf. PhSeOTf[9] and PhSOTf[10] also activated **2** with moderate efficiency (Entries 6 and 7). Conventional activators, such as $BF_3{\cdot}Et_2O$,[7] NIS, NIS/TMSOTf, *t*-BuOCl, MeOTf,[6b] and Br_2,[6g] were inefficient (<14% yield in all cases) under similar reaction conditions.

The generality of the new activator was examined by employing various organotellurium compounds and electrophiles, and the results are summarized in Table 2. The reaction of acyl telluride **2** with substituted benzene derivatives proceeded smoothly to give the desired products in excellent yields (Entries 1–3). The 1,4-disubstituted product predominantly formed over the 1,2-disubstituted product in the reaction with methoxybenzene (Entry 2). Heteroaromatic compounds, such as thiophene, also reacted with **2** to give the 3-substituted product in good yield (Entry 4). The observed regioselectivities were consistent with those in the conventional Friedel–Crafts reaction, suggesting that the reaction indeed generated carbocationic species from organotellurium compounds. Carbazole-derived acyl telluride **6d** and alkyl tellurides **7e** and **8f** were also activated with PhTeOTf in the presence of **3** to give the desired products in moderate-to-good yields (Entries 5–7).

The synthetic efficiency was further examined in the polymer-end functionalization using polystyrene **9e**, which was prepared by living radical polymerization of styrene (30 equiv)

Table 2. Phenyltellanyl triflate mediated the Friedel–Crafts reaction[a]



Entry	Substrate	Nucleophile	Product	Yield/%
1	**2**	1,3-$(MeO)_2C_6H_4$	**4a**	92
2	**2**	$MeOC_6H_5$	**4b**	91[b]
3	**2**	1,3-$Me_2C_6H_4$	**4c**	94
4[c]	**2**	Thiophene	**5**	74
5	**6d**	**3**	**6g**	79
6	**7e**	**3**	**7g**	63[d]
7	**8f**	**3**	**8g**	74
8	**9e**	**3**[e]	**9g**	100[f]

[a]A substrate and a nucleophile (1.5 equiv) were treated with the activator prepared from 1 (0.55 equiv) and AgOTf (1.1 equiv) in CH_2Cl_2 at room temperature for 1 h. [b]The product formed as a 96:4 mixture of 1,4-isomers and 1,2-isomers. [c]2,6-Di-*tert*-butyl-4-methylpyridine (1.5 equiv) was added to avoid decomposition of **5**. [d]Dialkylated product formed in 14% yield. [e]10 equiv of **3** was used. [f]Polystyrene with $M_n = 3400$, $M_w/M_n = 1.14$. See text for details for the efficiency of the end functionalization.

with **7e** (Entry 8).[5a] Thus, **9e** was treated with PhTeOTf in the presence of **3** (10 equiv). The gel permeation chromatography of the purified polymer **9g** indicated the formation of a monodisperse polystyrene with a number-averaged molecular weight (M_n) of 3440 and a molecular weight distribution (M_w/M_n, where M_w is the weight-averaged molecular weight) of 1.14. The ^1H NMR analysis revealed the nearly quantitative efficiency (97%) of the end-group transformation. MALDI-TOF mass spectrometry also indicated the predominant formation of **9g** together with a small amount of **10** as judged from a series of molecular ion peaks (Figure 1, **9g**:**10** = 93:7). The formation of **10** is also consistent with the generation of carbocationic species at the polymer-end.

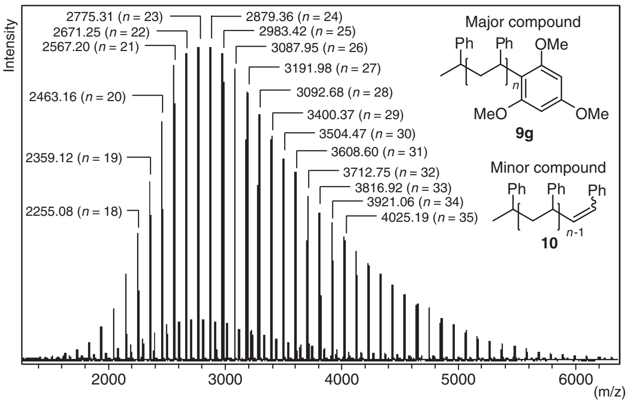


Figure 1. MALDI-TOF mass spectrum of polystyrene **9g** and **10** (=93:7). A series of peaks, as indicated by the average mass number, was observed in the silver ion added form $(M + Ag)^+$.

To confirm the activating species, the intermediate was analyzed by ^{125}Te NMR spectroscopy. While **1** did not show ^{125}Te NMR resonance in CD_2Cl_2 at room temperature,[8] a new signal at 1119 ppm appeared upon treatment of **1** with 2 equiv of AgOTf at 0 °C. The signal at 1155 ppm was also observed when dichlorophenyl(phenyltellanyl)telluride was treated with AgOTf.[11] These results, combined with the established protocol for the halogen–triflate exchange reaction using AgOTf, strongly suggest the formation of PhTeOTf as the activating species. However, attempts to isolate the intermediate have so far been unsuccessful. Further synthetic and mechanistic studies are underway, and will be reported in due course.

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11 The marginal difference of the chemical shift might be due to the interaction of PhTeOTf with AgX (X = Br or Cl).

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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