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Synthesis and Structure of Diaryltellurium Disulfonates and Their Application for the α-Tosyloxylation of Ketones

Yuga Shibuya, Hajime Kuruma, Makoto Oba, and Shinichi Koguchi*

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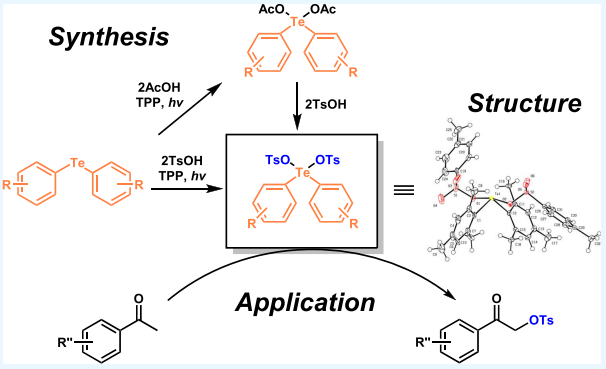
ABSTRACT: A concise and efficient synthetic route to a variety of functionalized diaryltellurium disulfonates (**1**) is presented. The hydrolysis of these diaryltellurium disulfonates (**1**) produces diarylhydroxytelluronium triflates (**2**). The molecular structures of the diaryltellurium disulfonates and diarylhydroxytelluronium triflates were determined unambiguously using single-crystal X-ray diffraction analysis. To the best of our knowledge, this represents one of the very few reports on the solid-state structures of diaryltellurium disulfonates and diarylhydroxytelluronium triflates to date. The utility of the thus obtained diaryltellurium disulfonates was subsequently demonstrated via their application to the α-tosyloxylation of ketones, which also marks the first use of this class of compounds for this transformation.



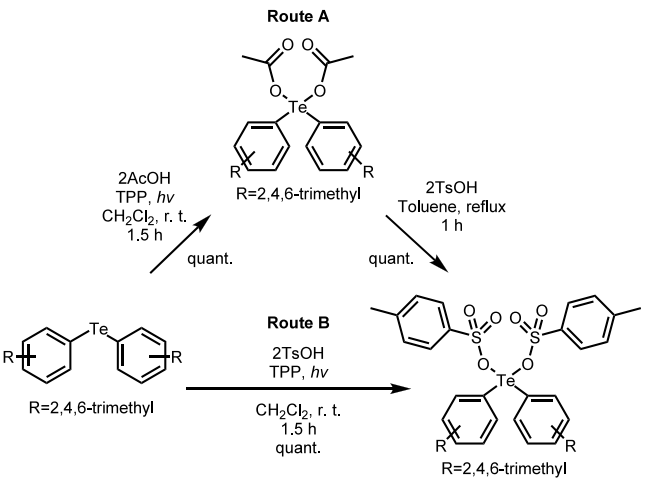
INTRODUCTION

The chalcogen element tellurium often exhibits unique structural features and properties. Organotellurium compounds have been found to exist in various oxidation states and several hypervalent states.[1] Accordingly, research in this area has traditionally been focused on the structure and physical properties of organic tellurium compounds. However, in recent years, research focus has shifted onto various applications of organotellurium compounds in organic reactions. For example, Togni and co-workers have reported a compound obtained from modifying the Togni reagent, which is a hypervalent iodine reagent, with a tellurium compound.[2] However, there are still only few reports detailing the synthesis of new hypervalent tellurium compounds and using them in organic transformations. Diaryltellurides, which have been a research focus of our group, also form various oxidation states and hypervalent compounds. We have previously demonstrated that diaryltellurides have the potential to be used in various organic reactions. So far, we have reported a synthetic route to new diaryltelluride derivatives,[3] the oxidation of organic compounds using such diaryltelluride derivatives,[4] the synthesis of diaryltellurium dicarboxylates and their subsequent use for the epoxidation of olefins,[5] and the structural analysis of complex organic tellurium compounds.[6] Here, we report on the relatively underexplored diaryltellurium disulfonates. Diaryltellurium disulfonates were first reported by the Tamagaki et al.[7] and Ogura et al.[8] more than 30 years ago. However, neither of these reports includes detailed characterization, X-ray crystallography, or applications. Therefore, to explore this class of compounds in depth, we first developed an efficient synthetic route to diaryltellurium disulfonates.

RESULTS AND DISCUSSION

Synthesis of Diaryltellurium Disulfonates. We developed two methods for the synthesis of diaryltellurium disulfonates from diaryltelluride substrates (Scheme 1),

Scheme 1. Synthesis of Diaryltellurium Disulfonates



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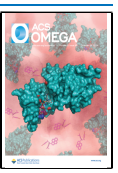

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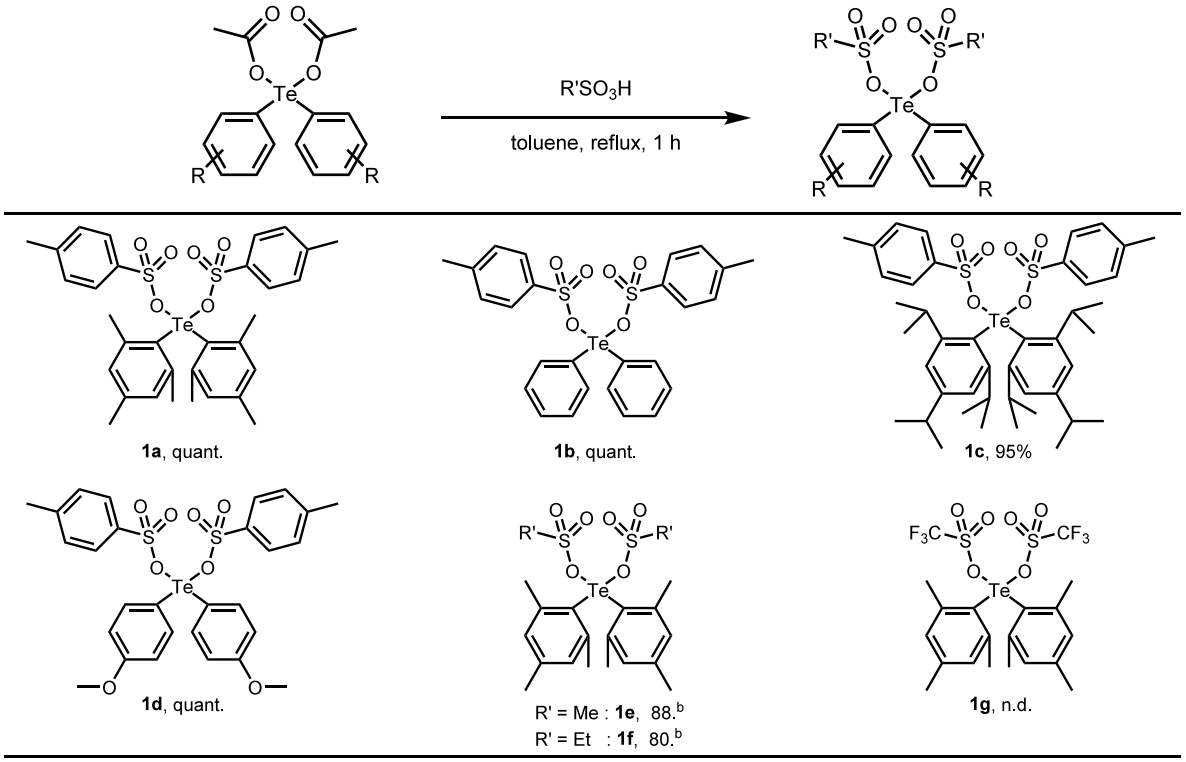
Table 1. Substrate Scope of the Reaction[a]



[a]Conditions: Diaryltellurium diacetate (1.0 mmol), R′SO_3H (2.0 mmol) and toluene (10 mL) under reflux conditions for 1 h. Isolated yield. [b]NMR yield.

which can be efficiently obtained under mild conditions via our previously developed cross-coupling of diaryldditellurides and arylboronic acids using copper thiophene-2-carboxylates (Scheme 1).[3]

The first method involves the synthesis of diaryltellurium dicarboxylates (Route A) followed by reaction with sulfonic acid. The second method is a one-pot reaction in which photooxidation with air and reaction with sulfonic acid are performed simultaneously (Route B). The first step in Route A is our previously reported method, which can be used to efficiently synthesize various diaryltellurium dicarboxylates.[9] Subsequent reaction of the formed diaryltellurium dicarboxylates with sulfonic acid allowed easy access to the corresponding diaryltellurium disulfonates in good yield. In contrast, Route B is a one-pot method that involves photooxidation with air and sulfonation.

Although this method provides the disulfonates in one step, it is then very difficult to separate the diaryltellurium disulfonates from the photosensitizer. The reaction also produces water, which may hydrolyze the diaryltellurium disulfonates, reducing the yield of the product. On the other hand, in Route A, water is removed due to the reaction conditions in refluxing toluene. It should be noted here that when Route B is performed in refluxing toluene, the diaryltellurium disulfonates are not obtained. We therefore chose Route A, which is a stepwise but efficient synthesis method, for our subsequent investigations. This reaction was carried out in methylene chloride containing molecular sieves (4-A). As a result, the yield of diaryltellurium disulfonates was 38%. (In addition, diarylhydroxytelluronium sulfonates were also confirmed at about 60% yelds.) Next, we examined the substrate scope for the formation of diaryltellurium disulfonates from diaryltellurium dicarboxylates (Table 1). When dimesityltelluride diacetate, diphenyltelluride diacetate or bis(methoxyphenyl)telluride diacetate were treated with *p*-toluenesulfonic acid, the corresponding diaryltellurium disulfonates (**1a**, **1b**, and **1d**) were obtained in good yield. The yield of the product (**1c**) from the reaction of bis(diisopropylphenyl)telluride diacetate and *p*-toluenesulfonic acid was slightly reduced. Next, the reactions of various sulfonic acids with diaryltellurium dicarboxylates were investigated. The reactions of methanesulfonic acid and ethanesulfonic acid with dimesityltelluride diacetate gave the corresponding diaryltellurium disulfonates (**1e** and **1f**) in about 80% yield. The byproduct of this reaction was thought to be a hydrolyzate. These compounds could not be isolated by column chromatography, albeit that a part of them could be crystallized, and their structures were characterized using X-ray crystallography. On the other hand, the reactions of trifluoromethanesulfonic acid with diaryltellurium dicarboxylates did not provide the corresponding products. It was difficult to isolate the compound (**1g**) because the trifluoromethanesulfonyl group quickly left. Diaryltellurium disulfonates (**1** to **1f**) can be stored in their solid state at room temperature for several weeks, but when dissolved in a solvent such as chloroform, they decompose within about a day. Various diaryltellurium disulfonates were rapidly hydrolyzed using water to prepare diarylhydroxytelluronium sulfonate. (The hydrolyzate of Compound **1b** was a complex mixture and the target product could not be confirmed.) (Scheme 2). To the best of our knowledge, there is only one report on the detailed structural analysis of diarylhydroxytelluronium sulfonates; Beckmann et al. have reported the synthesis of an intramolecularly coordinated diarylhydroxytelluronium sulfo-

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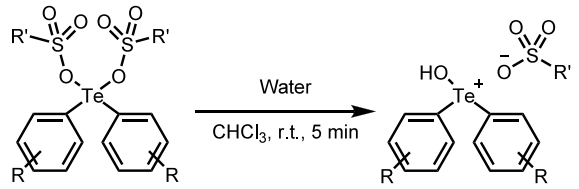
Scheme 2. Diaryltellurium Disulfonate Hydrolosis Reaction



R=2,4,6-trimethyl, R'=4-Tol	:**1a**	R=2,4,6-trimethyl, R'=4-Tol	:**2a**	82%
R=H, R'=4-Tol	:**1b**	R=H, R'=4-Tol	:**2b**	n.d.
R=2,4,6-trimethyl, R'=Me	:**1e**	R=2,4,6-trimethyl, R'=Me	:**2e**	quant.
R=2,4,6-trimethyl, R'=Et	:**1f**	R=2,4,6-trimethyl, R'=Et	:**2f**	76%

nate along with its X-ray crystal structure and theoretical calculations.[10] In recent years, diarylhydroxytelluronium sulfonate like chalcogenonium salts have begun to be used in various syntheses.[11] The structures of the diaryltellurium disulfonates and diarylhydroxytelluronium sulfonate obtained in this study were determined by X-ray crystallography.

Single-Crystal X-ray Diffraction Analysis of Diaryltellurium Disulfonates and Their Hydrolysates. Colorless crystals of diaryltellurium disulfonates **1a** Figure 1, **1e**, and

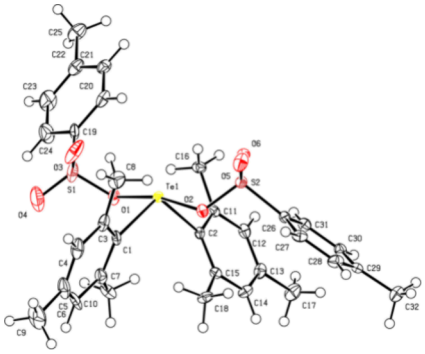


Figure 1. Solid-state structure of dimesityl tellanediyl bis(4-methylbenzenesulfonate) (**1a**) with thermal ellipsoids at 60% probability; selected bond distances (Å) and angles (°): Te1−C1, 2.114(3); Te1−C2, 2.131(3); Te1−O1, 2.148(2); Te1−O2, 2.179(2); Te1···O3, 3.001; Te1···O6, 3.069; O1−Te1−O2, 168.47(10); C1−Te1−C2, 110.25(14); C1−Te1−O1, 88.26(12); C1−Te1−O2, 85.11(11); C2−Te1−O1, 87.56(11); C2−Te1−O2, 85.91(11); O3···Te1···O6, 125.176.

1f suitable for single-crystal X-ray diffraction analysis were collected following the slow cooling of hot toluene solutions of **1a**, **1e**, and **1f**. Crystals of diarylhydroxytelluronium sulfonates **2a**, **2e**, and **2f**, which are the hydrolyzates of these diaryltellurium disulfonates, were collected following the slow diffusion of *n*-hexane into their respective chloroform solutions at room temperature.

Diaryltellurium disulfonates adopt a trigonal bipyramidal structure derived from their hypervalency. Specifically, the sulfonate groups are located at apical positions, and the aryl groups are located at equatorial positions. Selected bond distances and angles for the diaryltellurium disulfonates are summarized in Table 2. These structures are similar to those of our previously reported diaryltellurium dicarboxylate structures.[9]

The molecular structure of **2a** as a representative diarylhydroxytelluronium sulfonate is shown in Figure 2. In the case of **2a**, the diarylhydroxytelluronium cation has an overhanging tellurium atom derived from the shape of the diaryltellurium

Table 2. Relevant Te Bond Lengths and Angles of Diaryltellurium Disulfonates 1a, 1e, and 1f[a]

bond length (Å) or angle (°)	1a	1e	1f
Te−O1 length (shorter)	2.149	2.149	2.168
Te−O2 length (longer)	2.180	2.182	2.168
Te−C1 length (shorter)	2.115	2.107	2.118
Te−C2 length (longer)	2.134	2.122	2.118
O1−Te−O2 angle	168.5	166.0	169.28
C1−Te−C2 angle	110.2	111.5	107.03

[a]The molecular structure of **1a** as a representative diaryltellurium disulfonate is shown in the first figure.

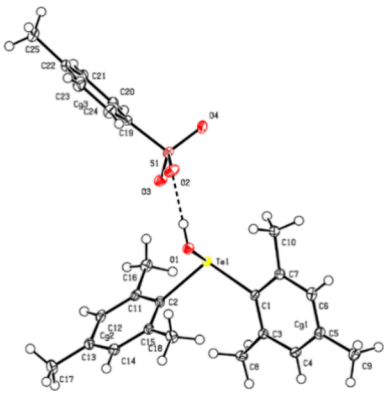


Figure 2. Structure of hydroxy dimesityl telluronium 4-methylbenzenesulfonate (**2a**) with thermal ellipsoids at 60% probability; selected bond distances (Å) and angles (°): Te1−C1, 2.1294(19); Te1−C2, 2.1300(19); Te1−O1, 1.9360(13); Te1···O3, 3.248; C1−Te1−C2, 106.03(7); C1−Te1−O1, 92.72(6); C2−Te1−O1, 90.40(7).

disulfonates. It consists of a diarylhydroxytelluronium cation and triflate anion that are associated by medium-to-strong hydrogen bonding, as indicated by the O···O donor−acceptor distance of 2.696 Å. Selected bond distances, angles, and O···O donor−acceptor distances for diarylhydroxytelluronium triflates **2a**, **2e**, and **2f** are summarized in Table 3. These

Table 3. Relevant Te Bond Lengths and Angles of Diarylhydroxytellurium Triflates 2a, 2e, and 2f[a]

bond length (Å), angle (°), or distance (Å)	2a	2e	2f
Te−O1 length	1.937	1.949	1.948
Te−C1 length (shorter)	2.129	2.123	2.122
Te−C1 length (longer)	2.130	2.135	2.131
C1−Te−C2 angle	106.0	106.8	108.6
O−O donor−acceptor distance	2.696	2.736	2.727

[a]2.1294(19); Te1−C2, 2.1300(19); Te1−O1, 1.9360(13); Te1···O3, 3.248; C1−Te1−C2, 106.03(7); C1−Te1−O1, 92.72(6); C2−Te1−O1, 90.40(7).

diarylhydroxytelluronium triflates exhibit similar structures, and especially their O···O donor−acceptor distances suggest that comparable medium-to-strong hydrogen bonding is present in all of them.[12]

Applications of Diaryltellurium Disulfonates in the α-Tosyloxylation of Ketones. We then investigated the α-tosyloxylation of ketones as a model application for the obtained diaryltellurium disulfonates. The α-tosyloxylation of ketones has been accomplished using the hypervalent iodine reagent [hydroxy(tosyloxy)iodo] benzene (HTIB). The first

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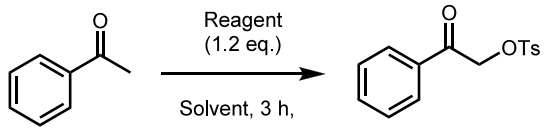
example of an α-tosyloxylation using HTIB was reported by the group of Nabana and Togo;[13] subsequently, the in situ generation of HTIB has also been investigated, and Yamamoto and Togo have reported the catalytic formation of HTIB when studying the synthesis of α-tosyloxyketone.[14] Yusubov and Wirth have conducted a solvent-free α-tosyloxylation of dicarbonyl compounds including 1,3-diketones via the in situ generation of HTIB using (diacetoxyiodo)benzene and *p*-toluenesulfonic acid monohydrate.[15] However, all reports to date for the synthesis of HTIB require the use of an oxidizing agent such as m-CPBA. On the other hand, as already mentioned, diaryltellurium disulfonates have the advantage that they can be synthesized using atmospheric oxygen. Regardless, their use in α-tosyloxylation transformations remains unprecedented to date.

We investigated the model α-tosyloxylation of acetophenone using diaryltellurium sulfonates under various reaction conditions. This reaction requires a somewhat high reaction temperature. When the reaction was carried out in refluxing solvents with a low boiling point, the tosyloxylation hardly progressed (Table 4, entries 1−3). (The boiling points of chloroform, acetonitrile, and benzene are 61.2 °C, 82 °C, and 80 °C, respectively.) On the other hand, when the high-boiling-point solvents toluene and xylene were used, the desired product was obtained in good yield (Table 4, entries 4 and 5). (The boiling points of toluene and xylene are 110.6 and 139 °C, respectively.) However, when xylene was used, the reaction temperature was so high that a small amount of decomposition was observed (Table 4, entry 5). When the reaction was carried out using toluene at room temperature, no product was obtained (Table 4, entry 6). Dimesityltellanediyl bis(4-methylbenzenesulfonate) (**1a**) was selected as the tosylation agent based on our previous studies due to its high stability and clear structure as determined by X-ray crystallography. When **1b**, in which the aryl group of the diaryltellurium disulfonate is a phenyl group, was used in this reaction, the product could not be obtained (Table 4, entry 7) When comparing **1a**−**c**, we observed that both **1b** and **1c** exhibit high reactivity, while **1b** is characterized by low reactivity. In contrast to **1a** and **1c**, which contain a substituent at the ortho position, **1b** has no substituent(s) on the benzene ring. Previous studies have shown that the presence of a substituent at the ortho position suppresses the formation of oligomers due to steric hindranc. On the other hand, it has been proposed that in the absence of and ortho substituent, e.g., in **1b**, oligomers are formed, leading to a decrease in reactivity (Table 4, entries 4, 7, and 8). Subsequently, we investigated the scope of applicable acetophenone derivatives using the newly established optimal reaction conditions, and the results are summarized in Table 5. Overall, the reactions proceeded rapidly and furnished the expected oxides in good-to-moderate yield. A decrease in yield was observed in the reaction of 2′-methylacetophenone, most likely due to steric hindrance. A plausible reaction pathway for the present reaction is shown in Scheme 3. We carried out the tosylation

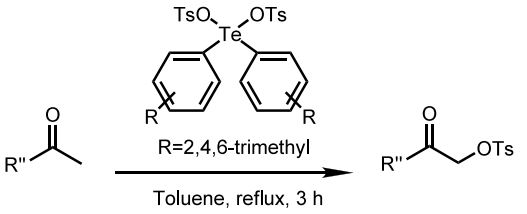
Table 4. Tosyloxylation of Acetophenone Using Diaryl Tellurium Sulfonates[a]

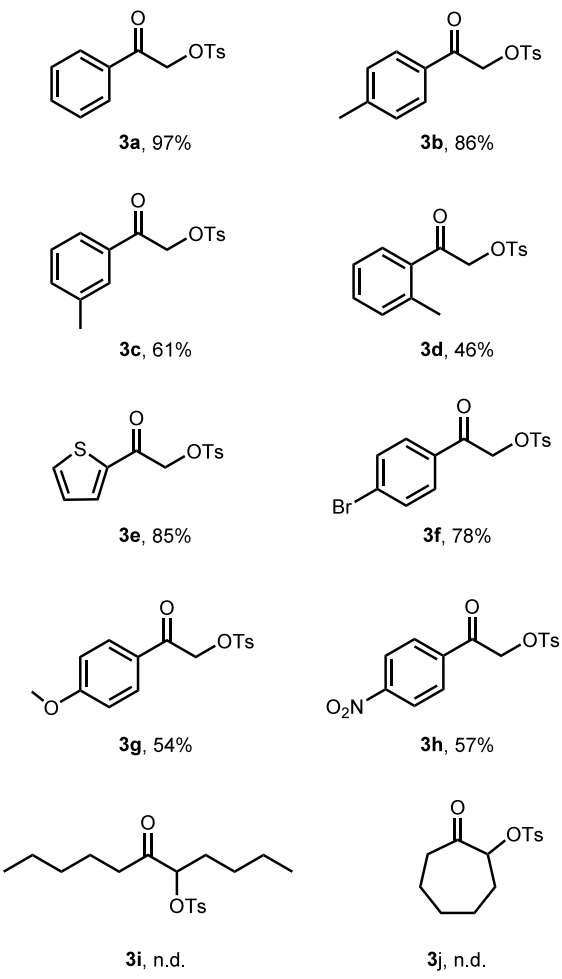


entry	reagent	solvent	condition	yield (%)[b]
1	**1a**	$CHCl_3$	reflux	n.r.
2	**1a**	MeCN	reflux	trace
3	**1a**	benzene	reflux	trace
4	**1a**	toluene	reflux	quant.
5	**1a**	xylene	reflux	63
6	**1a**	toluene	r.t.	n.r.
7	**1b**	toluene	reflux	trace
8	**1c**	toluene	reflux	83

[a]Conditions: Acetophenone (0.25 mmol), diaryltellurium ditosylates (0.30 mmol), solvent (2 mL), 3 h. [b]Isolated yield.

Table 5. Substrate Scope for the Tosyloxylation of Ketones Using 1a[a]





[a]Conditions: acetophenone derivatives (0.25 mmol), dimesityltellurium ditosylates (0.30 mmol), and toluene (2 mL), under reflux conditions for 3 h. Isolated yied.

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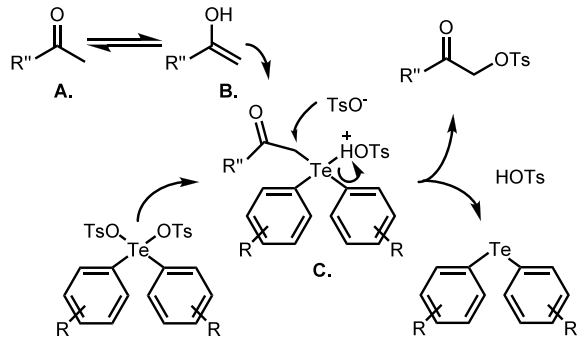
Scheme 3. (A−C) Plausible Reaction Pathway for the α-Tosyloxylation



of higher alkyl ketones using diaryltellurium disulfonates. As a result, the tosylation of alkyl ketones (**3h** and **3j**) did not proceed. (Although the consumption of the substrate was confirmed, no product was obtained, and the reaction mixture was obtained.) The mechanism of this reaction is thought to be similar to that of the tosylation of ketones using Koser's reagent.

CONCLUSIONS

We have developed a synthesis route to a series of diaryltellurium disulfonates from diaryltellurium dicarboxylates under safe and mild reaction conditions using atmospheric oxygen and inexpensive sulfonic acid. We structurally characterized multiple diaryltellurium disulfonates and their corresponding hydrolyzates. Furthermore, we discovered that these diaryltellurium disulfonates can be used for the α-tosyloxylation of acetophenone derivatives. It is expected that the findings presented herein will lead to new research areas that employ hypervalent organotellurium compounds in the future.

EXPERIMENTAL SECTION

General Information. All reagents and chemicals received from commercial suppliers were of reagent grade and were used unmodified. NMR spectra were performed on Bruker Advance DRX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{125}Te: 158 MHz) spectrometers. Deuterated solvents used are indicated in each case. All of the chemical shifts are reported as δ values (ppm) relative to TMS (δH 0.00), the central peak of deuteriochloroform (δC 77.16) and dimesitylteluride (δTe 275) unless otherwise noted; *J* values are expressed in hertz. The mass analyses were performed using a JEOL Accu TOF LC-plus JMS-T100LP spectrometer. The courses of the reactions were monitored using TLC aluminum sheets with silica gel 60 F254 (Merck). The column chromatography was performed using CHROMATOREX PSQ 60B (FUJI SILYSIA CHEMICAL Ltd.).

General Procedure for the Synthesis of Diaryltellurium Disulfonates (1). Toluene (10 mL) solution of diaryltellurium diacetate (0.1 mmol) and *p*-toluenesulfonate (0.2 mmol) were stirred under reflux conditions for 1 h. The mixture was evaporated.

General Procedure for Tosyloxylation of Ketones (3). Toluene (2 mL) solution of dimesityltellurium ditosylates (0.3 mmol) and acetophenone derivatives (0.25 mmol) were stirred under reflux conditions for 3 h. After the TLC of reaction mixture showed complete consumption of acetophenone derivatives, the mixture was evaporated, and the product was purified by silicagel column chromatography.

*Dimesityl-tellanediyl Bis(4-methylbenzenesulfonate) (**1a**).* Yield: 0.0351 g, (0.088 mmol 89%); white solid. m.p. = 149−153 °C. dec ^{1}HNMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 6H), 2.30(s, 6H), 2.33(s, 6H),2.83(s,6H),6.75(s,2H), 7.00(d, *J* = 8.0, 4H)7.02 (s, 2H) 7.26(d, *J* = 8.2, 4H) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1,21.4 22.6, 24.1, 126.3, 128.9, 130.4, 131.1, 133.1, 136.9, 142.4, 142.8, 143.0, 144.5. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 1193.9. HRMS (DART): *m*/*z* [M-TsO]$^+$ calcd for C25H29O3STe: 539.0895; found: 539.0936.

*Diphenyl-tellanediyl Bis(4-methylbenzenesulfonate) (**1b**).* Yield: 0.0563 g, (0.116 mmol quant.); white solid. m.p. = 133 °C. dec ^{1}H NMR (500 MHz, CDC_{l3}): δ = 2.36 (s, 6H), 7.13(d, *J* = 8.0, 4H), 7.45−7.55 (m, 10H), 7.76 (d, *J* = 8.0, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 126.5, 129.5, 130.4, 132.7, 133.7, 134.4, 137.2, 143.1. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 1203.9. HRMS (DART): *m*/*z* [M-TsO]$^+$ calcd for C19H17O3STe: 454.9956; found: 454.9983.

*Bis(2,6-diisopropylphenyl)-tellanediyl Bis(4-methylbenzenesulfonate) (**1c**).* Yield: 0.0409 g, (0.086 mmol 86%); white solid. m.p. = 85−93 °C. dec ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.5, 12H), 1.09 (d, *J* = 6.5, 12H), 2.34 (s, 6H) 3.19 (sept, *J* = 6.5, 4H) 7.13 (d, *J* = 8.0 4H) 7.28 (d, *J* = 7.7, 4H) 7.48 (t, *J* = 7.7, 2H) 7.68(d, *J* = 8.1, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 24.2, 24.9, 35.5, 126.3, 127.0, 129.0, 132.7, 133.1, 139.8, 141.3, 153.6. ^{125}Te NMR (157 MHz, $CDCl_3$): δ = 1212.9. HRMS (DART): *m*/*z* [M-TsO]$^+$ calcd for C31H41O3STe: 623.1834; found: 623.1888.

*Dis(4-methoxyphenyl)-tellanediyl Bis(4-methylbenzenesulfonate) (**1d**).* Yield: 0.0375 g, (0.082 mmol 82%): m.p. = 129−137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37(s, 6H), 3.84 (s, 6H), 6.95 (d, *J* = 9.1, 4H), 7.15(d, *J* = 8.0, 4H) 7.51 (d, *J* = 8.0, 4H), 7.67 (d, *J* = 9.0, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 55.7, 115.9, 124.5, 126.6, 129.5, 135.5, 143.0, 163.0. ^{125}Te NMR (157 MHz, $CDCl_3$): δ = 1232.1 HRMS (DART): *m*/*z* [M-C_6H_4OMe]$^+$ calcd for C21H21O7S2Te: 578.9786; found: 578.9653.

*Dimesityl-tellanediyl Dimethanesulfonate (**1e**).* Yield: 0.4451 g, (0.80 mmol, quant.); white solid, m.p. = 142−144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 6H), 2.44 (s, 6H), 2.52 (s, 6H), 2.89 (s, 6H), 7.10 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 22.9, 24.2, 39.2, 131.0, 131.4, 133.0, 143.1, 143.5, 144.2. ^{125}Te NMR (157 MHz, $CDCl_3$): δ = 1216.6 HRMS (DART): *m*/*z* [M-SO_3Me]$^+$ calcd for C19H25O3STe: 463.0582; found: 463.0612.

*Dimesityl-tellanediyl Diethanesulfonate (**1f**).* Yield: 0.1170 g, (0.20 mmol, quant.); white solid, m.p. = 158−163 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (m, 6H), 2.35 (s, 6H), 2.43 (s, 6H), 2.66 (m, 4H), 2.90 (s, 6H), 7.09(s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.5, 21.3, 23.1, 24.3, 46.6, 131.0, 131.3, 143.0, 143.3, 144.4. ^{125}Te NMR (157 MHz, $CDCl_3$): δ = 1212.3 HRMS (DART): *m*/*z* [M-SO_3Et]$^+$ calcd for C20H27O3STe: 477.0738; found: 477.0722.

*Hydroxydimesityl-tellaneyl 4-Methylbenzenesulfonate (**2a**).* Yield: 0.6092 g, (1.10 mmol, quant.); white solid, m.p. = 207−214 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29(m, 9H), 2.50 (s, 12H), 6.95−6.94 (m, 6H), 7.25−7.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 21.4, 22.8, 125.9, 128.5, 129.4, 131.2, 140.1, 140.9, 142.9, 143.4. HRMS (DART): *m*/*z* [M-OTs]$^+$ calcd for C18H23OTe: 385.0806; found: 385.0760.

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*Hydroxydimesityl-tellaneyl Methanesulfonate (**2e**).* Yield: 0.5259 g, (0.94 mmol, 94%); white solid, m.p. = 230−234 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26−2.29 (m, 9H), 2.39 (s, 12H), 6.98 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 22.4, 38.8, 130.7, 141.7, 143.1. HRMS (DART): m/z [M-SO_3Me]$^+$ calcd for C18H23OTe: 385.0806; found: 385.0802.

*Hydroxydimesityl-tellaneyl Ethanesulfonate (**2f**).* Yield: 0.5521 g, (0.76 mmol, 76%); white solid, m.p. = 223−225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (m, 3H), 2.30 (s, 6H), 2.50 (s, 12H), 2.73 (m, 2H), 6.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.0, 21.2, 22.6, 45.8, 131.0, 131.3, 143.0, 143.3. HRMS (DART): m/z [M−OH]$^+$ calcd for C20H27O3STe: 477.0738; found: 477.0765.

*α-Tosyloxyacetophenone (**3a**).* Yield: 0.0704 g, (0.24 mmol 97%); yellow solid. m.p. = 92−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 5.27 (s, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.84 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 70.1, 128.1, 128.2, 129.0, 130.0, 132.7, 133.8, 134.3, 145.4, 190.4. HRMS (DART): m/z [M + H]$^+$ calcd for C15H14O4S: 291.0686; found: 291.0708.

*α-Tosyloxy-p-methylacetophenone (**3b**).* Yield: 0.0647 g, (0.22 mmol 86%); white solid. m.p. = 84−88 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.43 (s, 3H), 5.23 (s, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 70.0, 128.1, 128.2, 129.6, 130.0, 131.3, 132.7, 145.3, 145.4, 189.9. HRMS (DART): m/z [M + H]$^+$ calcd for C16H16O4S: 305.0843; found: 305.0861.

*α-Tosyloxy-m-methylacetophenone (**3c**).* Yield: 0.0471 g, (0.15 mmol 61%); white solid. m.p. = 62−63 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.45 (s, 3H), 5.26 (s, 2H), 7.34−7.37 (m, 3H), 7.42 (d, J = 7.6 Hz, 1H), 7.62−7.64 (m, 2H), 7.86 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 21.7, 69.9, 125.2, 128.2, 128.5, 128.8, 129.9, 132.7, 133.8, 135.0, 138.9, 145.29, 190.4. HRMS (APCI): m/z [M + H]$^+$ calcd for C16H16O4S: 305.0843; found: 305.0837.

*α-Tosyloxy-o-methylacetophenone (**3d**).* Yield: 0.0343 g, (0.12 mmol 46%); white solid. m.p. = 54−56 °C. ^{1}H NMR (500 MHz, $CDCl^3$): δ = 2.43 (s, 3H), 2.44 (s, 3H), 5.12 (s, 2H), 7.23−7.26 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.39−7.50 (m, 2H), 7.81(d, J = 8.3 Hz,2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 21.7, 70.9, 125.8, 128.1, 128.5, 130.0, 132.3, 132.5, 132.7, 133.7, 139.4, 145.3, 193.7. HRMS (DART): m/z [M + H]$^+$ calcd for C16H16O4S: 305.0842; found: 305.0856.

*2-Oxo-2-(thiophen-2-yl)ethyl 4-Methylbenzenesulfonate (**3e**).* Yield: 0.0061 g, (0.21 mmol 85%); white solid. m.p. = 88−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 5.10 (s, 2H), 7.14−7.16 (m, 1H), 7.35 (d, J = 7.9 Hz, 2H), 7.71−7.79 (m, 2H), 7.84 (d, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 69.9, 128.2, 128.5, 130.0, 132.4, 133.2, 135.2, 140.0, 145.5, 183.7. HRMS (APCI): m/z [M + H]$^+$ calcd for C13H12O4S2:297.0250; found: 297.0248.

*α-Tosyloxy-p-bromoacetophenone (**3f**).* Yield: 0.0731 g, (0.20 mmol 78%); white solid. m.p. = 115−123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 5.20 (s, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 70.0, 128.3, 129.7, 130.1, 132.4, 132.64, 145.6, 189.9. HRMS (APCI): m/z [M + H]$^+$ calcd for C15H13O4SBr: 368.9791; found: 370.9758.

*α-Tosyloxy-p-methoxyacetophenone (**3g**).* Yield: 0.0452 g, (0.14 mmol 54%); yellow solid. m.p. = 107−113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 3.88 (s, 3H), 5.20 (s, 2H), 6.93 (d, J = 9.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.82−7.86 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 55.7, 69.9, 114.3, 126.9, 128.3, 130.0, 130.6, 132.8, 145.4, 164.4, 188.9. HRMS (DART): m/z [M + H]$^+$ calcd for C16H16O5S: 321.0791; found: 321.0803.

*α-Tosyloxy-p-nitroacetophenone (**3h**).* Yield: 0.0480 g, (0.14 mmol 57%); white solid. m.p. = 125−132 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 5.23 (s, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H), 8.33 (d, J = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 70.0, 124.1, 128.2, 129.4, 130.06, 132.3, 138,2, 145.72, 150.8, 189.8. HRMS (DART): m/z [M + H]$^+$ calcd for C15H13O6NS: 336.0537; found: 336.0573.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c05880.

General remarks; experimental procedures; synthesis of diaryltellurium disulfonates and synthesis of tosyloxylation of ketones; reference; and NMR spectra of compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Shinichi Koguchi − *Department of Chemistry, Tokai University, Hiratsuka-shi, Kanagawa 259-1292, Japan;* orcid.org/0000-0002-4564-3961; Email: koguchi@tokai-u.jp

Authors

Yuga Shibuya − *Department of Chemistry, Tokai University, Hiratsuka-shi, Kanagawa 259-1292, Japan*

Hajime Kuruma − *Department of Chemistry, Tokai University, Hiratsuka-shi, Kanagawa 259-1292, Japan*

Makoto Oba − *Department of Bioengineering, Tokai University, Hiratsuka-shi, Kanagawa 259-1292, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.4c05880

Notes

The authors declare no competing financial interest.

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