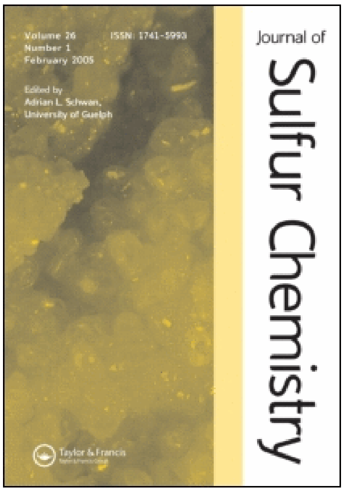

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Palladium-catalyzed Mizoroki–Heck-type reactions of chalcogenonium trifluoromethanesulfonates

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

The reaction of dimethyl(4-methylphenyl)selenonium trifluoromethanesulfonate with butyl acrylate proceeded in the presence of palladium(II) catalyst and silver acetate to give a Mizoroki–Heck-type product. The corresponding sulfonium salt also reacted with butyl acrylate to afford the same product under similar conditions, although the yields were low. In the case of the corresponding telluronium salt, the reaction proceeded smoothly to give a good yield.

Keywords: chalcogenonium salt; palladium(II) catalyst; Mizoroki–Heck-type reaction; silver acetate

1. Introduction

Carbon–carbon bond-forming reactions catalyzed by palladium complexes are a useful means of synthesizing natural products and materials (*1–4*). In the presence of palladium catalysts, organic halides react with alkenes to afford substituted alkenes (Mizoroki–Heck reaction) (*5–7*). Instead of organic halides, various organometallic reagents can also be used in the palladium-catalyzed reactions of alkenes to give the same type of products as those obtained by the Mizoroki–Heck reaction (*8–14*).

Palladium-catalyzed reactions of organotellurium compounds have also been investigated (*15, 16*), and the Mizoroki–Heck-type reactions of diorganotellurides and organotellurium(IV) compounds ($RTeCl_3$ and R_2TeCl_2) have been reported (*17, 18*). We have also found that telluronium salts reacted with alkenes to give Mizoroki–Heck-type products (*19*). On the contrary, to the best of our knowledge, little is known about the palladium-catalyzed reactions of organosulfur and selenium compounds with alkenes (*20*). In the course of our studies, we examined the reactivities of palladium-catalyzed reactions of chalcogenonium salts, such as sulfonium and selenonium salts.

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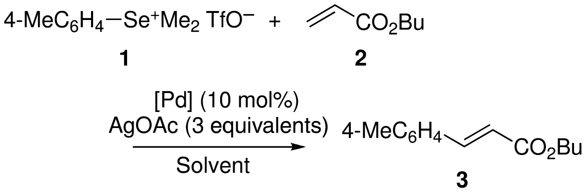
2. Results and discussion

The reactions of dimethyl(4-methylphenyl)selenonium trifluoromethanesulfonate (**1**) with butyl acrylate (**2**) were examined in the presence of palladium(II) catalysts and 3 equivalent amounts of silver acetate. The reaction, in the presence of 10 mol% $PdCl_2$, slightly proceeded at 50 °C to afford a trace amount of *trans*-butyl 3-(4-methylphenyl)propenoate (**3**) (Table 1, Entry 1), whereas in the case of telluronium salts, Mizoroki–Heck-type product **3** was obtained in good yield under the same conditions (*19*). The reaction also gave a trace amount of **3** in benzonitrile at 100 °C (Entry 2). When the reaction was carried out in N,N-dimethylformamide (DMF) at 150 °C, product **3** was obtained in 21% yield (Entry 3). In these reactions, only the *trans*-isomer was obtained. When palladium catalysts possessing a bidentate phosphine ligand, such as $PdCl_2$(dppe) and $PdCl_2$(dppb), were used, the yields of **3** were nearly equal to that when $PdCl_2$ was used (Entries 4 and 5). On the other hand, when a palladium catalyst having a monodentate triphenylphosphine ligand was used, product **3** was produced in 32% yield (Entry 6). It was reported that the organic groups of phosphine ligands could react with alkenes in the presence of palladium catalysts (*21*, *22*). In the cases of palladium–phosphine complexes, butyl cinnamate was also formed in the present reactions (Entries 4–6). When bipyridine ligand was used instead of phosphine ligands, **3** was afforded in 38% yield (Entry 7).

When the reaction of a corresponding sulfonium salt **4** was carried out by using $PdCl_2$ at 100 °C in benzonitrile or at 150 °C in DMF, the formation of a trace amount of Mizoroki–Heck-type product **3** was detected from the ^{1}H-NMR spectra in both cases (Table 2, Entries 1 and 2). The reactions of **4** were also examined in the presence of various palladium complexes at 150 °C in DMF. In all cases, product **3** was obtained, although the yields were very low (Entries 3–6). In the cases of Entries 3–5, butyl cinnamate was also produced in good yield, based on phosphine ligands. Thus, the reactivity of sulfonium trifluoromethanesulfonate **4** is lower than that of the corresponding selenonium salt **1** in the present reactions. In the Mizoroki–Heck-type reactions of organometallic reagents and telluronium salts, it is known that the reactions go forward by way of transmetallation (*8–14*, *19*). The present reactions of selenonium and sulfonium salts were also considered to proceed through a similar reaction pathway. So far, even sulfonium salt, whose

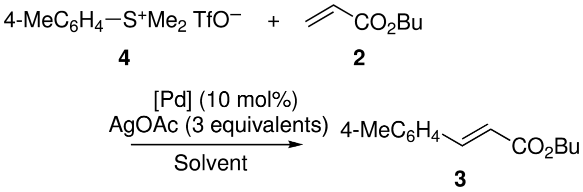
Table 1. Mizoroki–Heck-type reaction of selenonium salt.



Entry	[Pd]	Solvent	Temp (°C)	Time (h)	Yield (%)
1	$PdCl_2$	CH_3CN	50	42	Trace
2	$PdCl_2$	C_6H_5CN	100	42	Trace
3	$PdCl_2$	DMF	150	6	21
4[a]	$PdCl_2$(dppe)	DMF	150	6	19
5[b]	$PdCl_2$(dppb)	DMF	150	6	19
6[c]	$PdCl_2(PPh_3)_2$	DMF	150	6	32
7	$PdCl_2$(bpy)	DMF	150	6	38

Notes: [a]Butyl cinnamate was also obtained in 4% yield based on the substrate, and in 10% based on dppe. [b]Butyl cinnamate: 3% (based on the substrate), 8% (based on dppb). [c]Butyl cinnamate: 16% (based on the substrate), 27% (based on PPh_3).

Table 2. Mizoroki-Heck-type reaction of sulfonium salt.



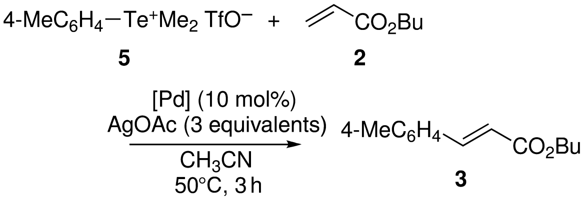
Entry	[Pd]	Solvent	Temp (°C)	Time (h)	Yield (%)
1	$PdCl_2$	C_6H_5CN	100	168	Trace
2	$PdCl_2$	DMF	150	24	Trace
3[a]	$PdCl_2(PPh_3)_2$	DMF	150	24	Trace
4[b]	$PdCl_2$(dppe)	DMF	150	24	5
5[c]	$PdCl_2$(dppb)	DMF	150	24	2
6	$PdCl_2$(bpy)	DMF	150	24	3

Notes: [a]Butyl cinnamate was also obtained in 31% yield based on the substrate, and in 52% based on PPh_3. [b]Butyl cinnamate: 34% (based on the substrate), 85% (based on dppe). [c]Butyl cinnamate: 24% (based on the substrate), 60% (based on dppb).

center atom has higher electronegativity than tellurium and selenium, was found to react with the alkene in the presence of palladium(II) complexes, although the yields were very low.

To compare the reactivities of the chalcogenonium salts, the reactions of telluronium salt **5** having the same substituents and counter anion were examined. The reaction of telluronium salt **5** with **2** in the presence of 10 mol% $PdCl_2$ and the additive smoothly proceeded even at 50 °C, and the reaction was completed within 3 h to give an 83% yield of desired product **3** (Table 3, Entry 1). Tellurium possesses the lowest electronegativity (highest metallic property) among chalcogen elements, and carbon–tellurium bonds are weaker than the corresponding carbon–selenium and carbon–sulfur bonds. Thus, telluronium salt **5** might react with alkene **2** under milder conditions. Use of other palladium(II) catalysts, such as $PdCl_2(PPh_3)_2$, $PdCl_2$(dppe), $PdCl_2$(dppb), and $PdCl_2$(bpy), also afforded Mizoroki–Heck-type product **3** in good to excellent yields, while some cases yielded a small amount of butyl cinnamate as well (Entries 2 and 4).

Table 3. Mizoroki-Heck-type reaction of telluronium salt.



Entry	[Pd]	Yield (%)
1	$PdCl_2$	83
2[a]	$PdCl_2(PPh_3)_2$	72
3	$PdCl_2$(dppe)	100
4[b]	dCl_2(dppb)	93
5	$PdCl_2$(bpy)	68

Notes: [a]Butyl cinnamate was also obtained in 6% yield based on the substrate, and in 10% based on PPh_3. [b]Butyl cinnamate: trace.

3. Experimental

3.1. *Preparation of dimethyl(4-methylphenyl)chalcogenonium trifluoromethanesulfonates*

General procedure. To a tetrahydrofuran (THF) solution (30 mL) of 4-methylphenylmagnesium bromide that was prepared from 4-bromotoluene (3.70 mL, 30.0 mmol) and magnesium turnings (0.73 g, 30.0 mmol) was added sulfur (0.96 g, 30.0 mmol), selenium (2.37 g, 30.0 mmol), or tellurium powder (3.80 g, 30.0 mmol) by portions at room temperature. The mixture was stirred for 1 h at room temperature. To the resulting mixture was added methyl iodide (1.87 mL, 30.0 mmol) at room temperature, and stirring was continued for 1 h. The resulting solution was poured into 1 M HCl aq/Et_2O (20 mL/20 mL) and the organic layer was separated. The aqueous layer was extracted with Et_2O. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by distillation to give the corresponding methyl(4-methylphenyl)chalcogenide (S: 73%, Se: 75%, Te: 81%). To a dichloromethane solution (30 mL) of the chalcogenide (ca. 22 mmol) were added 1.5 equivalent amounts of methyl iodide and silver triflate. The mixture was stirred for 3 h at room temperature. The white precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give the corresponding chalcogenonium trifluoromethanesulfonate.

3.1.1. *Dimethyl(4-methylphenyl)selenonium trifluoromethanesulfonate (**1**)*

82%; mp 116–117 °C (decomp); ^1H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.14 (s, 6H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 25.0, 120.4 (q, $J = 320$ Hz), 122.1, 129.7, 131.6, 144.0; IR (KBr) 3020, 1271, 1233, 1176, 1153, 1029, 813 cm^{-1}. Anal. Calcd for $C_{10}H_{13}F_3O_3SSe$: C, 34.39; H, 3.75; found: C, 34.17; H, 3.65.

3.1.2. *Dimethyl(4-methylphenyl)sulfonium trifluoromethanesulfonate (**4**)*

92%; mp 92–94 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.34 (s, 6H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.2, 120.4 (q, $J = 319$ Hz), 121.0, 129.5, 131.7, 145.9; IR (KBr) 3026, 2938, 1595, 1429, 1256, 1171, 1031, 817, 759 cm^{-1}. Anal. Calcd for $C_{10}H_{13}F_3O_3S_2$: C, 39.73; H, 4.33; found: C, 39.25; H, 4.25.

3.1.3. *Dimethyl(4-methylphenyl)telluronium trifluoromethanesulfonate (**5**)*

86%; mp 121–122 °C (decomp); ^1H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.62 (s, 6H), 7.32 (d, $J = 7.9$ Hz, 2H), 7.59 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.5, 21.4, 115.9, 120.2 (q, $J = 317$ Hz), 131.2, 133.3, 142.7; IR (KBr) 3000, 1240, 1176, 1034, 840, 799, 645 cm^{-1}. Anal. Calcd for $C_{10}H_{13}F_3O_3STe$: C, 30.19; H, 3.29; found: C, 29.94; H, 3.20.

3.2. *General procedure for the Mizoroki–Heck-type reaction of a chalcogenonium salt with butyl acrylate*

Chalcogenonium salt (1.00 mmol), palladium catalyst (0.10 mmol), and silver acetate (0.50 g, 3.00 mmol) were placed in a dried screw-capped glass tube and solvent (4.0 mL) was added. Butyl acrylate (0.13 g, 1.00 mmol) was added to the solution. The mixture was stirred for the desired period at the desired temperature. The reaction mixture was diluted with Et_2O and then was passed briefly through a silica gel pad. The pad was washed with Et_2O and the eluate was washed with 1 M HCl aq (15 mL). The aqueous layer was extracted with Et_2O. The combined organic layer was washed with saturated $NaHCO_3$ aq and then with brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane as eluent) to afford corresponding product **3** and/or butyl cinnamate.

3.2.1. *Trans-Butyl 3-(4-methylphenyl)propenoate (**3**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (t, $J = 7.4$ Hz, 3H), 1.45 (m, 2H), 1.69 (m, 2H), 2.36 (s, 3H), 4.20 (t, $J = 6.5$ Hz, 2H), 6.42 (d, $J = 15.5$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 15.5$ Hz, 1H) (*23*).

3.2.2. *Butyl cinnamate (23)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.44 (m, 2H), 1.70 (m, 2H), 4.21 (t, $J = 6.7$ Hz, 2H), 6.44 (d, $J = 16.0$ Hz, 1H), 7.33–7.42 (m, 3H), 7.51–7.54 (m, 2H), 7.68 (d, $J = 16.0$ Hz, 1H).

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