

Palladium-Catalyzed Mizoroki–Heck-type Reactions Using Telluronium Salts

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A Mizoroki–Heck-type reaction of telluronium iodides with olefins proceeded under mild conditions to produce substituted olefins in high yields. The reaction required a catalytic amount of palladium(II) species and a stoichiometric amount of silver(I) acetate as an additive.

Carbon–carbon bond-forming reactions using palladium catalysts are useful means of synthesizing natural products and materials.¹ It is well known that the Mizoroki–Heck (MH) reactions of organic halides with olefins in the presence of palladium catalyst afford substituted olefins.² Recently, it was found that organometallic compounds, such as boron,³ silicon,⁴ tin,⁵ and other organometallic reagents,⁶ instead of organic halides also reacted with olefins to produce the same products as obtained by the MH reaction. These reactions are called MH type reactions.

Various organometallic reagents have been investigated to use palladium-catalyzed coupling reactions. Tellurium compounds can be also used as organometallic reagents, because tellurium atom possesses metallic properties. However, to the best of our knowledge, only organic tellurides or organotellurium(IV) compounds (R_2TeCl_2 or $RTeCl_3$) were used in palladium-catalyzed coupling reactions.⁸ On the other hand, we have been studying the synthesis and stereochemistry of telluronium salts.⁷ In the course of our studies, we focused on the application of telluronium salts to organic synthesis because, until now, telluronium salts have not been used in transition-metal-catalyzed reactions. Telluronium salts are more stable compounds and can be stored for a few months in the air, therefore telluronium salts can be used as convenient organometallic reagents. We investigated the palladium-catalyzed MH type reaction using telluronium salts, and the results are described herein.

When the reaction of dimethylphenyltelluronium iodide (**1a**) with butyl acrylate was carried out in the presence of a catalytic amount of $Pd(OAc)_2$ (10 mol %) in CH_3CN at 50 °C for 24 h, (*E*)-butyl 3-phenylpropenoate (**2a**) was produced. However, the amount of product was almost the same as the amount of palladium catalyst employed (7%). On the other hand, palladium(0) catalyst, such as $Pd(PPh_3)_4$, was not effective in this reaction. Thus, the reaction requires a Pd(II) complex. Next, when 4.0 equiv. of $AgOAc$ was used as an additive, **2a** formed in excellent yield even though a catalytic amount of $Pd(OAc)_2$ was used (Table 1, Entry 1). When the reaction was carried out in THF, **2a** was also produced in high yield (Entry 2). Although the reaction proceeded using a more polar solvent such as DMF or nonpolar solvent such as toluene or hexane, the reaction required a longer reaction time for completion (Entries 3–5). The reaction also occurred using $PdCl_2$ to produce **2a** in excellent yields after 1 h (Entry 6). When the reaction was carried out using other palladium catalysts possessing phosphine ligands, such as $PdCl_2(PPh_3)_2$, longer reaction time was required (24 h) and

Table 1. Reaction of dimethylphenyltelluronium iodide (**1a**) with butyl acrylate in the presence of palladium catalyst^a

$PhTe^+Me_2I^- + \text{olefin} \xrightarrow[\text{solvent, 50 } ^\circ\text{C}]{[Pd] (10 \text{ mol } \%), AgOAc (4 \text{ mmol})} Ph-CH=CH-R$				
1a	R : CO_2Bu			2a
Entry	[Pd]	Solvent	Time/h	Yield/% ^b
1	$Pd(OAc)_2$	CH_3CN	6	99
2	$Pd(OAc)_2$	THF	8	93
3	$Pd(OAc)_2$	DMF	24	97
4	$Pd(OAc)_2$	toluene	48	77
5	$Pd(OAc)_2$	hexane	48	67
6	$PdCl_2$	CH_3CN	1	97
7	$PdCl_2(PPh_3)_2$	CH_3CN	24	56

^aAll reactions were carried out using **1a** (1.0 mmol), butyl acrylate (1.0 mmol), [Pd] (10 mol %), and $AgOAc$ (4.0 mmol).

^bDetermined by GC analysis.

the yield decreased (Entry 7). Thus, phosphine ligands inhibit the reaction.

The reaction of **1a** with butyl acrylate was carried out in CH_3CN at 50 °C in the presence of various amounts of $AgOAc$. When 3.0 equiv. of $AgOAc$ were used, the reaction proceeded successfully to give **2a** in 94% yield after 1 h, however, when 2.0 or 1.0 equiv. of $AgOAc$ were used, the yields decreased even though after 24 h (45%, 19%). These results indicate that this reaction requires at least 3.0 equiv. of $AgOAc$.⁹

The MH type reactions of various aryltelluronium iodides with olefins were studied under the optimized conditions (Table 2). Telluronium salt **1a** reacted with various olefins possessing electron-withdrawing or neutral groups to give the corresponding products in good yields. The reactions of telluronium salts **1b** and **1c**, which possess an electron-donating group at the 4-position of the aryl group, proceeded to give the products in high yields (Entries 6 and 7), whereas, the reaction using telluronium salts **1d** afforded the product in a slightly lower yield (Entry 8). In the case of telluronium salts possessing methyl or methoxy group at the 2-position, such as **1e** and **1f**, longer reaction times were required (Entries 9 and 10). The reactions of telluronium salts **1g** and **1h** afforded the corresponding products in 72% and 66% yields, respectively (Entries 11 and 12). These results indicated that, at least, two phenyl groups on telluronium salts were used in the present reaction. On the other hand, when alkenyltelluronium salts such as dimethylstyryltelluronium iodide was used, homocoupling reaction instead of the MH type reaction occurred and 1,4-diphenyl-1,3-butadiene was given in 81% yield.

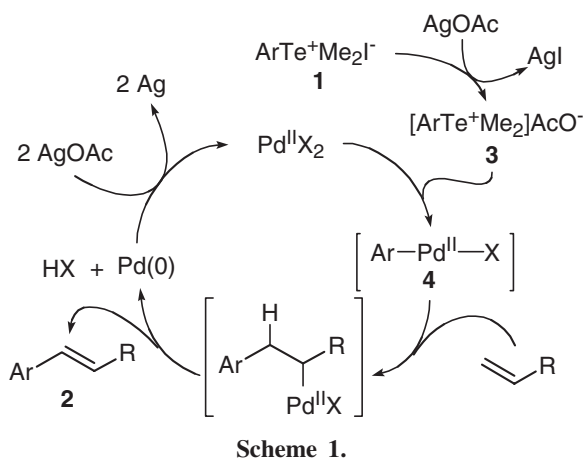
It was noteworthy that purification of this reaction product was very easy. When the MH type reactions were carried out us-

ing organic tellurides, the crude mixture must be purified to remove unreacted organic telluride in some cases. On the other hand, in the case of the present reaction using telluronium salts, the pure product was obtained by only filtration using silica gel to remove solids in the reaction mixture.

Table 2. The MH type reaction of aryltelluronium iodides **1**^a

$\text{Ar}_n\text{Te}^+\text{Me}_{(3-n)}\text{I}^- + \text{CH}_2=\text{CH}-\text{R} \xrightarrow[\text{CH}_3\text{CN}, 50^\circ\text{C}]{\text{PdCl}_2 (10 \text{ mol } \%), \text{AgOAc} (3 \text{ mmol})} \text{Ar}-\text{CH}=\text{CH}-\text{R}$					
Entry	Ar	n	R	Time/h	Yield/% ^b
1	Ph (1a)	1	CO ₂ Bu	3	94
2	1a	1	CN	6	63
3	1a	1	CHO	7	82
4	1a	1	COMe	7	80
5	1a	1	Ph	6	86
6	4-MeC ₆ H ₄ (1b)	1	CO ₂ Bu	3	95
7	4-MeOC ₆ H ₄ (1c)	1	CO ₂ Bu	3	95
8	4-CF ₃ C ₆ H ₄ (1d)	1	CO ₂ Bu	3	73
9	2-MeC ₆ H ₄ (1e)	1	CO ₂ Bu	12	55
10	2-MeOC ₆ H ₄ (1f)	1	CO ₂ Bu	12	70
11	Ph (1g)	2	CO ₂ Bu	120	72 ^{c,d}
12	Ph (1h)	3	CO ₂ Bu	120	66 ^{c,e}

^aAll reactions were carried out using **1** (1.0 mmol), olefin (1.0 mmol), PdCl₂ (10 mol %), and AgOAc (3.0 mmol), unless otherwise noted. ^bIsolated yields. ^cYields were based on olefins. ^d**1g** (0.5 mmol) was used. ^e**1h** (0.33 mmol) was used.



A plausible mechanism of the MH type reaction of telluronium salts is shown in Scheme 1. As mentioned above, since this reaction only occurred when using Pd(II) catalyst, arylpalladium species **4** will be formed by transmetalation of tellurium compound with Pd(II) compounds. After arylpalladium species **4** is produced, the reaction proceeds in a similar manner to that in other MH type reactions to give the product **2**. Because this reaction needs 3 equiv. of AgOAc, AgOAc plays two roles in the present reaction. Firstly, 2 equiv. of AgOAc act as oxidant that reproduces the Pd(II) species. Secondly, 1 equiv. of AgOAc exchanges the counter-anions of telluronium salts from iodide to acetate. Thus, AgOAc is converted to Ag(0) and AgI.¹⁰

In summary, the palladium-catalyzed MH type reaction of telluronium salts was achieved. Because the workup of this reaction is very simple, and telluronium salts can be stored as solids for a few months in the air, this reaction is convenient.

References and Notes

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- When other silver salts and copper salts were used, the yields of the corresponding products were very low (<17%).
- Formation of Ag(0) and AgI was identified from reaction mixture by the X-ray diffraction (XRD). We attempted to survey the tellurium species after the reaction, but it could not be identified.