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Palladium-Catalyzed Coupling and Carbonylative Coupling of Silyloxy Compounds with Hypervalent Iodonium Salts

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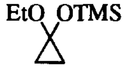
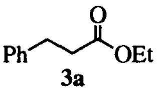
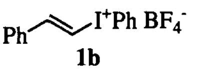
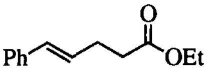
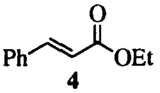
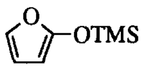
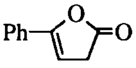
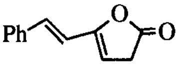
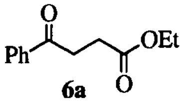
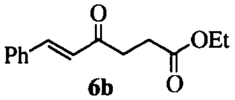
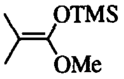
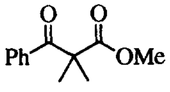
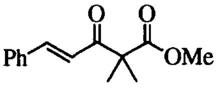
Abstract: *Arylation and alkenylation of 1-ethoxy-1-trimetylsilyloxycyclopropane with diphenyliodonium tetrafluoroborate and alkenyliodonium tetrafluoroborate were accomplished by slow addition of silyloxycyclopropane to iodonium salts in the presence of* Pd(OAc)$_2$ *(2 mol %) and* DME/H$_2$O *(4 : 1) to afford β-substituted ester. Alternatively, carbonylative coupling of silyloxypropane was carried out by slow addition of silyloxypropanes to iodonium salts under CO(1 atm) at room temperature in aqueous medium. The palladium-catalyzed coupling of ketene trimethylsilyl acetals with iodonium salts is also described.* © 1997 Elsevier Science Ltd. All rights reserved.

The palladium-catalyzed carbon chain elongation of aryl triflates using silyloxypropanes and carbonylative arylation *via* ester homoenolate have been well established by Nakamura and Kuwajima.[1] Alternatively, palladium-catalyzed coupling of ketene trimethylsilyl acetals with aryl triflates was utilized to prepare α-substituted esters.[2] In connection with our program to utilize hypervalent iodonium salts in palladium-catalyzed coupling reactions,[3] we have examined the palladium-catalyzed coupling and carbonylative coupling of silyloxy compounds with iodonium salts as substitutes for aryl triflates as electrophiles and have found that the coupled products obtained depend highly on the reaction conditions including the order of addition.

The palladium-catalyzed coupling of silyloxy compounds with iodonium tetrafluoroborates is summarized in Table 1. When the diphenyliodonium tetrafluoroborate (**1a**)[4] was coupled with [(1-ethoxycyclopropyl)oxy]trimethylsilane (**2a**)[5] in the presence of a Pd catalyst, we have found that the order of addition was crucial in the nature of the product formed. When a mixture of silyloxycyclopropane **2a** and iodonium salt **1a** in DME/H$_2$O (4 : 1) was stirred at 30-40 °C in the presence of Pd(OAc)$_2$ or Pd(PPh$_3$)$_4$ catalyst, a mixture of **3a** and **4** was obtained. However, slow addtion of silyloxycyclopropane **2a** in DME *via* a syringe pump at 30 °C for 1 h to a solution of iodonium salts **1a** in DME/H$_2$O (4 : 1) containing Pd(OAc)$_2$ (2 mol %), resulted in the formation of β-phenylated ester **3a**[6, 7a] as the sole product (Method A, entry 1 in Table 1).[8] It is reasoned that arylation could be accomplished with cationic organopalladium complex PhPd$^+$ BF$_4^-$ from iodonium salt **1a** followed by C-C bond cleavage of this strained silyloxypropane **2a**. By applying the same method, we could easily obtain γ,δ-unsaturated ester **3b**[7b] from alkenyliodonium

Table 1. Palladium-Catalyzed Coupling and Carbonylative Coupling of Siloxy Compounds with Hypervalent Iodonium Salts Under Aqueous Conditions[a]

Entry	Iodonium Salt	Siloxy Compound	Reaction Conditions	Time (min)	Product	Isolated Yield(%)[b]
1	$Ph_2I^+ BF_4^-$ **1a**	 **2a**	A	60	 **3a**	87
2	 **1b**	**2a**	A	60	 **3b**	91
3	**1a**	**2a**	B	30	 **4**	91
4	**1a**	 **2b**	C	30	 **5a**	89
5	**1b**	**2b**	C	30	 **5b**	85
6	**1a**	**2a**	D	60	 **6a**	81
7	**1b**	**2a**	D	60	 **6b**	76
8	**1a**	 **2c**	E	30	 **7a**	86
9	**1b**	**2c**	E	15	 **7b**	92

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[a] All the reactions were run with iodonium salts (1 equiv) in the presence of siloxy compounds (1.1 equiv). Reaction conditions A: $Pd(OAc)_2$ (2 mol %), iodonium salts (1 equiv), DME/H_2O (4 : 1), slow addition of siloxy compound in DME, 30 °C. B: $Pd(OAc)_2$(2 mol %), siloxy compounds (1 equiv), DME, 30 °C, 15 min, then addition of iodonium salt (1 equiv) in DME/H_2O (4 : 1). C: $Pd(OAc)_2$ (2 mol %), iodonium salts (1 equiv), siloxy compounds (1 equiv), DME/H_2O (4 : 1), 30 °C. D: $Pd(OAc)_2$ (2 mol %), iodonium salts (1 equiv), CO (1 atm), DME/H_2O (4 : 1), slow addition of siloxy compound (1 equiv) in DME, 30 °C. E: $Pd(OAc)_2$(2 mol %), iodonium salts (1 equiv), siloxy compounds (1 equiv), CO (1 atm), DME/H_2O (4 : 1), 30 °C. [b] The yields are isolated yields.

salts **1b**[4] (entry 2). Alternatively, β-aryl-substituted unsaturated ester **4**[6] could be prepared by inverse addition of iodonium salt **1a** to a solution of silyloxycyclopropane **2a** in DME and $Pd(OAc)_2$(2 mol %) in 91% yield (Method B, entry 3).[8] It is presumed that under these conditions the intermediate ethyl acrylate formed by β-elimination of the homoenolate ($AcOPdCH_2CH_2CO_2Et$) from silyloxycyclopropane and $Pd(OAc)_2$ is subjected to Heck reaction with the iodonium salt **1a**.[9] It is notable that the coupling of iodonium salt **1a** with 2-(trimethylsilyloxy)furan (**2b**)[5] in DME/H_2O (4 : 1) at 30 °C afforded γ-phenyl-substituted β,γ-unsaturated butyrolactone **5a**[7c] as the only product in 89% yield (Method C, entry 4). The regioselectivity of **5a** could be explained by the isomerization of α,β-unsaturated butyrolactone initially formed to the β,γ-unsaturated lactone **5a** in the presence of palladium catalyst. Similarly, the reaction of alkenyliodonium salt **1b** gave **5b**[6] (entry 5). This cross-coupling was extended to carbonylative coupling under atmospheric pressure of carbon monoxide to get β–keto esters or γ–keto esters. We could obtain γ–keto ester **6a**[6, 7d] in 81% yield by slow addition of silyloxycyclopropane **2a** to the salt **1a** (as in Method A), under atmospheric pressure of carbon monoxide at 30 °C for 1 h (entry 6, Method D).[8] By similar method, δ,ε–unsaturated γ-keto ester **6b**[7e] was afforded (entry 7). Finally, ketene trimethylsilyl acetal **2c**[5] was successfully coupled with iodonium salts **1a** and **1b** to give β-keto esters **7a**[7f] and **7b**[6] in 86 and 92% yields, respectively (Method E, entry 8 and 9).

In conclusion, palladium-catalyzed cross-coupling and carbonylative cross-coupling of silyloxy compounds with hypervalent iodonium salts afforded aryl- or alkenyl-substituted esters or unsaturated esters depending on the reaction conditions under mild conditions.

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5. [(1-Ethoxycyclopropyl)oxy]trimethylsilane (**2a**), 2-(trimethylsilyloxy)furan (**2b**), and methyl trimethylsilyl dimethylketene acetal (**2c**) were purchased from Aldrich Chemical Co.

6. Satisfactory spectral and physical data were obtained for the new compounds in accord with the structure. Selected physical and spectral data are as follows. **3a**: TLC, SiO_2, EtOAc/hexanes = 1 : 10, R_f = 0.50. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3H, *J* = 7.13 Hz), 2.62 (t, 2H, *J* = 7.83 Hz), 2.95 (t, 2H, *J* = 7.83 Hz), 4.12 (q, 2H, *J* = 7.13 Hz), 7.22 (m, 3H), 7.32 (m, 2H). IR (neat) 3056, 2985, 1728, 1266 cm^{-1}. MS (m/e) 179, 178 (M^+), 107, 104 (base peak), 92. **4**: TLC, SiO_2, EtOAc/hexanes = 1 : 10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, 3H, *J* = 7.08 Hz), 4.27 (q, 2H, *J* = 7.08 Hz), 6.44 (d, 1H, *J* = 16.0 Hz), 7.39 (m, 3H), 7.53 (m, 2H), 7.69 (d, 1H, *J* = 16.0 Hz). IR (neat) 3057, 2985, 2306, 1709, 1639, 1450, 1368, 1266 cm^{-1}. MS (m/e) 177, 176 (M^+), 131 (base peak), 103, 78, 52. **5b**: TLC, SiO_2, EtOAc/hexanes = 1 : 2, R_f = 0.20. ^1H NMR (400 MHz, $CDCl_3$) δ 3.36 (d, 2H, *J* = 2.8 Hz), 5.45 (t, 1H, *J* = 2.8 Hz), 6.56 (d, 1H, *J* = 15.9 Hz), 7.03 (d, 1H, *J* = 15.9 Hz), 7.29 (m, 1H), 7.36 (m, 2H), 7.45 (m, 2H). IR (neat) 2925, 1795, 1111 cm^{-1}. MS (m/e) 188, 187, 186 (M^+, base peak), 158, 131, 103. **6a**: TLC, SiO_2, EtOAc/hexanes = 1 : 10, R_f = 0.26. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, 3H, *J* = 7.12 Hz), 2.75 (t, 2H, *J* = 6.65 Hz), 3.31 (t, 2H, *J* = 6.65 Hz), 4.15 (q, 2H, *J* = 7.12 Hz), 7.46 (m, 2H), 7.56 (m, 1H), 7.98 (m, 2H). IR (neat) 3058, 1732, 1688, 1265 cm^{-1}. MS (m/e) 207, 206 (M^+), 161, 105 (base peak), 77. **7b**: TLC, SiO_2, EtOAc/hexanes = 1 : 10, R_f = 0.37. ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 6H), 3.72 (s, 3H), 6.85 (d, 1H, *J* = 15.6 Hz), 7.40 (m, 3H), 7.55 (m, 2H), 7.72 (d, 1H, *J* = 15.6 Hz). IR (neat) 2985, 1738, 1693, 1615, 1446, 1265 cm^{-1}. MS (m/e) 232 (M^+), 131 (base peak), 103, 77.

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8. The typical procedure is as follows. Method A: To a mixture of diphenyliodonium tetrafluoroborate (**1a**)(500 mg, 1.36 mmol) and $Pd(OAc)_2$ (2 mol %, 6.1 mg) was added DME : H_2O (4 : 1)(5 mL) under nitrogen atmosphere and stirred at room temperature for 10 min and then was slowly added [(1-ethoxycyclopropyl)oxy]trimethylsilane (**2a**)(261 mg, 1.49 mmol) in DME (10 mL) *via* syringe pump for 1 h at 30 °C. The reaction mixture was extracted with ether (20 mL x 3) and the organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated in *vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/Hexanes = 1 : 10, R_f = 0.50) to give ethyl 3-phenyl propionate (**3a**)(211 mg, 87%). Method **B**: To a mixture of [(1-ethoxycyclopropyl)oxy]trimethylsilane (**2a**)(261 mg, 1.49 mmol) and $Pd(OAc)_2$ (2 mol %, 6.1 mg) was added DME (5 mL) under nitrogen atmosphere and stirred at 30 °C for 15 min and then was added diphenyliodonium tetrafluoroborate (**1a**)(500 mg, 1.36 mmol) in DME/H_2O (4 : 1)(10mL) and stirred for 15 min. The reaction mixture was extracted with ether (20 mL x 3) and the organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated in *vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/Hexanes = 1 : 10, R_f = 0.46) to give ethyl *trans*-cinnamate (**4**)(253 mg, 91%). Method **D**: To a mixture of diphenyliodonium tetrafluoroborate (**1a**)(500 mg, 1.36 mmol) and $Pd(OAc)_2$ (2 mol %, 6.1 mg) was added DME : H_2O (4 : 1)(5 mL) under atmospheric pressure of carbon monoxide and stirred at room temperature for 10 min and then was slowly added [(1-ethoxycyclopropyl)oxy]trimethylsilane (**2a**)(261 mg,1.49 mmol) in DME (10mL) *via* syringe pump for 1 h at 30 °C. The reaction mixture was extracted with ether (20 mL x 3) and the organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated in *vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/Hexanes = 1 : 10, R_f = 0.260) to give **6a** (227 mg, 81%).

9. As indirect evidence, when the silyloxycyclopropane **2a** was reacted with $Pd(OAc)_2$(2 mol %) in DME at 35 °C for 15 min, we could obtain ethyl acrylate in almost quantitative yield.

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