Palladium-Catalyzed Coupling between Organic Halides and Organotin Compounds Involving C-N Unsaturated Bonds at the Reaction Centers

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(Received September 19, 1985)

Synopsis. Imidoyl chlorides were good substrates which can react with a variety of organotin compounds to give ketimines in the presence of a catalytic amount of palladium complex. Under similar conditions, *C*-tributylstannyl imines did not give the products except with 2-(tributylstannyl)benzothiazole, -benzoxazole, and 1-methyl-2-(tributylstannyl)imidazole. And *N*-tributylstannyl imines could not be utilized.

The cross-coupling of organotin compounds with organic halides catalyzed by palladium complex is an important and versatile method of stereo- and regiospecific carbon–carbon bond formation.[1] Thus aryl and vinyl bromides are good substrates, and aryl- and vinyl-tin compounds are good reagents. From the structural analogy, imidoyl chlorides and stannyl imines are expected to be good substrates and reagents, respectively. This is further suggested by that imidoyl chloride undergoes the oxidative addition to the low valent palladium complex,[2] since such oxidative adducts are considered to be intermediates in the palladium-catalyzed coupling between organotins and halides. In this note, we report about possible utility of the following three types of reactions.

$$R^1CCl=NR^2 + n\text{-}Bu_3SnR^3 \xrightarrow{[Pd]} R^1R^3C=NR^2 + n\text{-}Bu_3SnCl$$

$$R^3X + n\text{-}Bu_3SnR^1C=NR^2 \xrightarrow{[Pd]} R^1R^3C=NR^2 + n\text{-}Bu_3SnX$$

$$R^3X + n\text{-}Bu_3SnN=CR^1R^2 \xrightarrow{[Pd]} R^3N=CR^1R^2 + n\text{-}Bu_3SnX$$

As for heterocycles containing C=N bonds, palladium-catalyzed couplings of 2-halobenzothiazole with organozinc compound are known.[3,4] We also applied the cross-coupling of tin compounds with halides to these heterocycle systems.

I. Palladium-Catalyzed Reaction of Imidoyl Chloride and Related Compound with Organotin Compounds. As is shown in Table 1, imidoyl chlorides were good substrates to give ketimines when treated with a variety of organotin compounds in the presence of a catalytic amount of palladium complex. Quite recently, we have found similar trials published.[5] The best yields were obtained when the reaction was carried out using a slightly excess amount of tin reagents and 1 mol% of dichlorobis(triphenylphosphine)-palladium at 120 °C for 20 h in xylene. Prolonged reaction time decreased the yield of the product. The reaction with acetonyltributyltin gave two products, that is, the acetonylated product (isomerized to conjugated enone) and the iso-propenylated one, though in relatively low yields.

In the reaction with tin enolate (α-stannyl ketone or enol stannyl ether), dichlorobis(tri-*o*-tolylphosphine)palladium was a better catalyst than dichlorobis-(triphenylphosphine)palladium, as in the case of cross-coupling of tin enolate with other organic halides.[6]

In allylation of *N*-(α-chlorobenzylidene)aniline, the product was isomerized to the conjugated imine which was identical to the product derived from the reaction with 1-propenyltributyltin. Although the stereochemistry of the product was not fully characterized, GLC analysis showed the mixture of *E*- and *Z*-isomer being produced.

II. Palladium-Catalyzed Reaction of Bromobenzene with Tributylstannyl Imines. There are two types of stannyl imines, *C*-stannyl imine and *N*-stannyl imine. The results of trials for the cross-coupling reaction of these stannyl imines with bromobenzene were summarized in Table 2.

C-Stannyl heterocycles, such as 2-(tributylstannyl)benzothiazole, -benzoxazole, and 1-methyl-2-(tributylstannyl)imidazole were found to be good reagents, while acyclic *C*-stannyl imine, *N*-[α-(tributylstannyl)-benzylidene]aniline and *N*-[1-(tributylstannyl)pentylidene]-*t*-butylamine did not react.

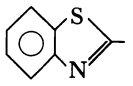
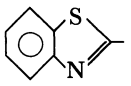
On the other hand, *N*-tributylstannyl imines could hardly be utilized in this type of reaction.

Experimental

^{1}H NMR spectra were taken on a Varian EM-360 spectrometer. IR spectra were obtained on Jasco A-100 spectrometer. MS spectra were taken by using JMS-07. GLC analyses were carried out with Ohkura 802 instrument, using columns (1.5 m) packed with 10% Silicone SE-30 and SF-96 on Celite 545. Bp and mp are uncorrected values. (1 mmHg=133.322Pa).

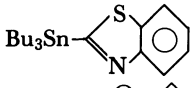
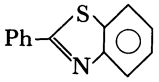
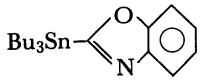
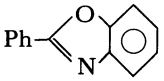
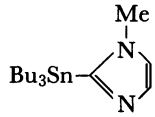
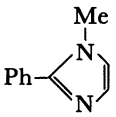
Materials. *N*-(α-Chlorobenzylidene)aniline (bp 110—115 °C/0.3 mmHg, mp 41 °C; lit,[7] bp 174—176 °C/12 mmHg, mp 41 °C) and 2-chlorobenzothiazole (bp 83.5 °C/1.4 mmHg; lit,[8] bp 135—136 °C) were prepared by the treatment of benzophenone oxime and benzothiazole with phosphorus pentachloride, respectively. $Bu_3SnCH_2CH=CH_2$,[9] $Bu_3SnCH=CH_2$,[10] $Bu_3SnCH=CHCH_3$,[11] Bu_3SnPh,[12] $Bu_3SnCH_2COCH_3$,[13] 1-cyclohexenoxytributyltin,[13] $Bu_3SnN=C(CCl_3)(OMe)$,[14] $Bu_3SnN=CPh(NEt_2)$,[15] and $Bu_3SnN=C=NSnBu_3$[16] were prepared according to the methods described in the literatures. 1-Methyl-2-(tributylstannyl)imidazole (bp 123—130 °C/0.3 mmHg), 2-(tributylstannyl)benzoxazole (bp 135—140 °C/0.15 mmHg), and 2-(tributylstannyl)benzothiazole (bp 144—146 °C/0.15 mmHg) were prepared by the treatment of 1-methylimidazole, benzoxazole, and benzothiazole with butyl lithium, followed by the addi-

Table 1. Pd-Catalyzed Reaction of *N*-(α-Chlorobenzylidene)aniline and 2-Chlorobenzothiazole with Organotin Compounds

R-Cl	R′-SnBu$_3$	Cat.[a]	Solvent	Time / h	Temp / °C	Product R-R′	Yield / %[b]
PhN=CPh-	CH_2=$CHCH_2$-	none	PhH	10	120	I[c]	0
		A	PhH	10	120	I	86
		B	PhH	10	120	I	71
		C	PhH	10	120	I	33
		D	PhH	10	120	I	0
		E	PhH	10	120	I	0
		A	THF	10	120	I	52
		A	DMSO	10	120	I	0
		A	HMPA	10	120	I	trace
		A	DMP	10	120	I	trace
		A	Xylene	42	80	I	56
		A	Xylene	20	100	I	65
		A	Xylene	10	120	I	85
		A	Xylene	20	120	I	91 (67)
		A	Xylene	40	120	I	56
PhN=CPh-	CH_2=CH-	A	Xylene	10	120	II	(67)
PhN=CPh-	CH_3CH=CH-	A	Xtlene	20	120	I	(87)
PhN=CPh-	Ph-	A	Xylene	60	120	III	(78)
PhN=CPh-		C	Xylene	5	120	IV	74
PhN=CPh-	MeCOCH_2-	C	Xylene	5	120	V[d] VI[e]	9 25
	Ph-	A	Xylene	20	120	VII	(86)
	CH_3CH=CH-	A	Xylene	20	120	VIII	(88)

a) A: $PdCl_2(PPh_3)_2$, B: $Pd(PPh_3)_4$, C: $PdCl_2[P(o\text{-tolyl})_3]_2$, D: $PdCl_2$+2 $P(OEt)_3$, E: $PdCl_2(PhCN)_2$. b) GLC yield based on the halide, isolated yield in parentheses. c) PhN=CPh(CHCHMe). d) PhNHCPh=CH(COMe) e) PhN=CPh(OCMe=CH_2).

Table 2. Pd-Catalyzed Reaction of Bromobenzene with Tributylstannyl Imines[a]

Stannyl Imine	Product		Isolated Yield/%
Bu_3Sn-CPh=NPh	Ph_2C=NPh		0
Bu_3Sn-CBu^n=NBu^t	$PhBu^nC$=NBu^t		0
		VII	56
		IX	75
		X	89
Bu_3Sn-N=C=N-$SnBu_3$	PhN=C=NPh		0
Bu_3Sn-N=CPh(NEt_2)	PhN=CPh(NEt_2)		0
Bu_3Sn-N=C(CCl_3)(OMe)	PhN=C(CCl_3)(OMe)		0

a) Reactions were carried out by using 1 mol% of $PdCl_2(PPh_3)_2$ in xylene at 120 °C for 20 h.

tion of tributyltin chloride, respectively. *N*-[1-(tributylstannyl)pentylidene]-*t*-butylamine (bp 120—122 °C/0.3 mmHg) was prepared by the insertion of butyl lithium into *t*-butyl isocyanide, then the addition of tributyltin chloride.[17] *N*-[α-(tributylstannyl)benzylidene]aniline (bp 148—155 °C/0.3 mmHg) was prepared by the reaction of *N*-(α-chlorobenzylidene)aniline with lithium tributylstannate(II). ^{1}H NMR spectra of these tin compounds showed reasonable structures of them which were used without further characterizations. Palladium complexes were already reported.[6]

Reaction Procedure. A mixture of halide (3.0 mmol), tin compound (3.6 mmol), and palladium complex (0.03 mmol) in xylene (6 ml) was heated under argon at 120 °C for 20 h. After washed with aqueous potassium fluoride to remove the tributyltin halide produced, organic layer was extracted with ether and dried over sodium sulfate. Then after evaporation of ether, the product was isolated by distillation or recrystallization.

Products. (I) Bp 110 °C/0.4 mmHg. ^{1}H NMR (CCl_4) δ=6.58—8.10 (m, 10H, phenyl), 5.52—6.35 (m, 2H, olefinic), 2.70 (d, *J*=7.0 Hz, 3H, methyl). IR (CCl_4) 1600 (C=N), 1650 and 1300 (C=C) cm^{-1}. MS *m/z* 221 (M^+). (II) Bp 95 °C/0.3 mmHg, mp 78—80 °C. ^{1}H NMR (CCl_4) δ=6.58—8.10 (m, 10H, phenyl) 5.24—6.65 (m, 3H, olefinic). IR (CCl_4) 1596 (C=N), 1630 (C=C) cm^{-1}. MS *m/z* 206 (M^+). (III) Mp 111—112 °C, lit,[18] 113 °C. ^{1}H NMR (CCl_4) δ=6.40—7.90 (m, phenyl). IR (KBr) 1598 (C=N) cm^{-1}. (IV) Bp 158 °C/0.4 mmHg. ^{1}H NMR (CCl_4) δ=6.11—8.38 (m, 10H, phenyl), 4.98 (s, 1H, olefinic), 0.68—2.67 (m, 8H, methylene). IR (CCl_4) 1600 (C=N), 1658 (C=C) cm^{-1}. MS *m/z* 278 (M^+). (V) GLC collection. ^{1}H NMR (CCl_4) δ=6.25—7.20 (m, 5H, *C*-phenyl), 7.30 (s, 5H, *N*-phenyl), 6.74 (s, 1H, olefinic), 2.12 (s, 3H, methyl), 5.29 (s, 1H, N-H). IR (CCl_4): 1620 (C=O), 1298(NH) cm^{-1}. (VI) GLC collection. ^{1}H NMR (CCl_4) δ=6.45—8.09 (m, 10H, phenyl), 1.82 (s, 3H, methyl), 4.10 (s, 2H, olefinic). IR (CCl_4) 1660 (C=N), 1640 (C=C) cm^{-1}. (VII) Mp 111—112 °C. Found: C 73.89, H 4.35, N 6.31%; Calcd for

$C_{13}H_9NS$: C 73.90, H 4.29, N 6.63%. (VIII) Mixtures of *E* and *Z*. *E* isomer: ^1H NMR (CCl_4) δ=6.91—8.08 (m, 4H, phenyl), 6.40—6.80 (m, 2H, olefinic), 1.92 (d, J=5 Hz, 3H, methyl). MS *m/z* 175 (M^+). *Z* isomer: ^1H NMR (CCl_4) δ=6.98—8.19 (m, 4H, phenyl), 5.72—6.43 (m, 2H, olefinic), 2.26 (d, J=6 Hz, 3H, methyl). MS *m/z* 175 (M^+). (IX) Mp 92—93 °C. ^1H NMR (CCl_4) δ=7.11—8.52 (m, phenyl). MS *m/z* 195 (M^+). Found: C 80.04, H 4.84, N 7.19%; Calcd for $C_{13}H_9ON$: C 79.98, H 4.65, N 7.17%. (X) bp 100 °C/0.35 mmHg. ^1H NMR (CCl_4) δ=7.09—7.60 (m, 5H, phenyl), 6.70 and 6.80 (s, 2H, olefinic), 3.51 (s, 3H, methyl). MS *m/z* 158 (M^+).

Financial support by Asahi Glass Foundation is gratefully acknowledged. We also thank Kohriyama Kasei Co. for a gift of tributyltin oxide.

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