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Palladium Catalyzed Iminocarbonylation of Bromobenzene with Isocyanide and Organotin Compounds

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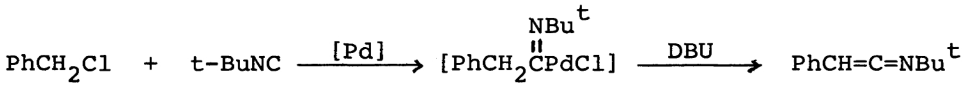
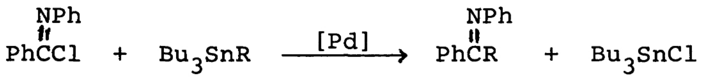
Palladium catalyzed reactions of ternary systems involving bromobenzene, t-butyl isocyanide, and organotin compounds were found to occur giving the corresponding imines, although the catalytic efficiencies were rather low.

Palladium catalyzed carbonylation of the organic halides-organotin compounds system is an important method to prepare unsymmetrical ketones.[1-3] On the other hand, isocyanide having a similar electronic structure to carbon monoxide has been hardly used in place of carbon monoxide. Ito et al. reported that ketenimine was formed by the reaction of isocyanide, benzyl chloride, and DBU(1,5-diazabicyclo[5.4.0]undec-5-ene) in the presence of a catalytic amount of palladium acetate in THF(tetrahydrofuran) at room temperature.[4] This has been interpreted by that the oxidative adduct of benzyl chloride to palladium(0) is inserted by isocyanide to form the iminoacylpalladium complex.



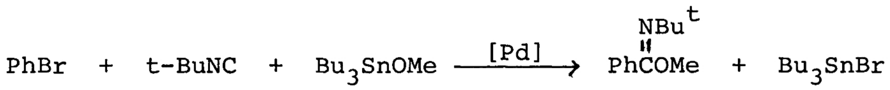
$$\mathrm{PhCH_2Cl} + t\text{-}\mathrm{BuNC} \xrightarrow{[\mathrm{Pd}]} [\mathrm{PhCH_2}\overset{\mathrm{NBu^t}}{\overset{\|}{\mathrm{C}}}\mathrm{PdCl}] \xrightarrow{\mathrm{DBU}} \mathrm{PhCH{=}C{=}NBu^t}$$

Meanwhile, we[5] and Tanaka et al.[6] have reported that imidoyl chloride reacts with organotin compounds in the presence of a catalytic amount of palladium complex to give the coupling products, imines. This reaction may also involve the iminoacylpalladium complex as an intermediate.



$$\mathrm{Ph}\overset{\mathrm{NPh}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + \mathrm{Bu_3SnR} \xrightarrow{[\mathrm{Pd}]} \mathrm{Ph}\overset{\mathrm{NPh}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{Bu_3SnCl}$$

Intermediary of iminoacylpalladium in the above two reaction systems prompted us to carry out palladium catalyzed reaction of ternary systems, composed of bromobenzene, t-butyl isocyanide, and organotin compounds, expecting to obtain imines, coupling products involving insertion of the isocyanide. Table 1 shows the results of several trials using tributyltin methoxide.



$$\mathrm{PhBr} + t\text{-}\mathrm{BuNC} + \mathrm{Bu_3SnOMe} \xrightarrow{[\mathrm{Pd}]} \mathrm{Ph}\overset{\mathrm{NBu^t}}{\overset{\|}{\mathrm{C}}}\mathrm{OMe} + \mathrm{Bu_3SnBr}$$

Table 1. Pd-catalyzed reaction of bromobenzene with t-butyl isocyanide and tributyltin methoxide

Entry No.	PhBr (mmol)	t-BuNC (mmol)	Bu_3SnOMe (mmol)	Catalyst[a] (mmol)	Temp °C	Time h	Solvent	Yield of PhC(=NBu^t)OMe/%[b]
1	1.0	3.0	1.2	A; 0.05	120	20	HMPA[c]	trace
2							DMF[d]	trace
3							DMSO[e]	trace
4							THF	14
5							PhH	29
6					80			trace
7					100			21
8					140			20
9		1.5			120			32
10		5.0						14
11		1.5		0.01				4
12				0.03				19
13				0.10				63
14				N; -				0
15				B; 0.10				0
16				C;				24
17				D;				0
18				E;				10
19				F;				21
20				G;				25

a) A; $Pd(PPh_3)_4$, B; $RhCl(PPh_3)_3$, C; $NiCl_2(PPh_3)_2$, D; $PdCl_2$, E; $PdCl_2(PhCN)_2$, F; $PdCl_2[P(o\text{-tolyl})_3]_2$, G; $PdCl_2(PPh_3)_2$, N; none.
b) GLC yield. c) Hexamethylphosphoric triamide. d) Dimethylformamide.
e) Dimethyl sulfoxide.

As Table 1 shows, the palladium catalyzed reaction of the ternary system actually occurred to give the expected iminoacyl ester. The most proper solvent was benzene (entry No. 1-5), and suitable temperatures were around 120 °C (entry

No. 5-8). Increased amounts of isocyanide resulted to decrease the yield of the product (entry No. 8-10). This may be due to the trend that isocyanide polymerize in the presence of transition metal complex (Pd, Ni, Co, etc.).[7)] Yield of the product also depends upon the concentration of the catalyst (entry No. 10-14), about ten mole percent of a catalyst being required for the production in moderate yield. This means that the catalytic efficiency is not high. And the most suitable catalyst examined was tetrakis(triphenylphosphine)palladium (entry No. 13-20).

We have examined the applicability of the reaction to other organotin compounds. Based on the results of Table 1, reaction conditions were chosen as follows, the mixtures of bromobenzene (1.0 mmol), t-butyl isocyanide (1.5 mmol), organotin compound (1.2 mmol), and tetrakis(triphenylphosphine)palladium (0.10 mmol) in benzene (1 cm^3) were sealed in a glass tube under vacuo, and heated at 120 °C for 20 h. The products were analyzed by GLC. The results were shown in Table 2.

Table 2. Pd-catalyzed reaction of bromobenzene with various organotin compounds and t-butyl isocyanide

Entry No.	Bu_3Sn-R	Product	Yield/%
1	-OMe	$PhC(=NBu^t)OMe$	63
2	-OEt	$PhC(=NBu^t)OEt$	48[a)]
3	$-NEt_2$	$PhC(=NBu^t)NEt_2$	22
4	-SPh	$PhC(=NBu^t)SPh$	10
5	$-CH_2CH=CH_2$	$PhC(=NBu^t)CH_2CH=CH_2$	trace
6	$-CH=CH_2$	$PhC(=NBu^t)CH=CH_2$	trace
7	$-C(OEt)=CH_2$	$PhC(=NBu^t)C(OEt)=CH_2$	30
8	$-C\equiv CPh$	$PhC(=NBu^t)C\equiv CPh$	52, 40[a)]
9	-CN	$PhC(=NBu^t)CN$	61[b)]
10	-Ph	$Ph_2C=NBu^t$	0
11	-H	$PhCH=NBu^t$	0

a) Isolated yield. b) Iodobenzene was used instead of bromobenzene.

Table 2 shows that there are some limitations in utilizable organotin compounds, and shows the tendency that the reaction takes place smoothly when organotin has a relatively polar Sn-R bond. This implies that the transition state of the key step involves a considerable charge developping on the atom attached to the tin.8) It should be noteworthy, however, that the reaction with α-ethoxyvinyltributyltin gave the product in 30% yield, while the reaction with vinyltributyltin did not.

The present work gave, in anyway, first example of the palladium catalyzed reaction of a ternary system, involving bromobenzene, t-butyl isocyanide, and an organotin compound, although there still remain the problems to be improved particularly in the catalytic efficiency and the limitation in utilizable organotin compounds.

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