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# THE REDUCTIVE COUPLING REACTION OF DIARYLIODONIUM SALTS CATALYZED BY PALLADIUM-ZINC SYSTEM[1]

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Biaryls are readily obtained in good yields by reductive coupling reactions of various diaryliodonium salts in the presence of zinc and a palladium catalyst under mild conditions.

The preparation of biaryls with haloarenes catalyzed by copper compounds have been well known as the Ullmann reaction.[2] Recently, the transition metal catalyzed coupling reaction of organic halides have provided a new approach to synthesis of biaryls.[3] On the other hand, Tamura and co-workers[4] reported that diaryliodonium salts react with a Grignard reagent, in the presence of nickel chloride, to give biaryls in good yields. However, this method is not practical because of limitations of utilizable diaryliodonium salts.

We now wish to report a more simple and convenient method for the synthesis of biaryls from diaryliodonium salts.[5] Thus, the reductive coupling reaction of diaryliodonium salts proceed catalytically in the presence of palladium compounds and a stoichiometric amount of zinc dust under mild conditions to give biaryls and iodoarenes in excellent yields (Eq.1).

$$2[\mathrm{Ar\text{-}\overset{+}{I}\text{-}Ar}]\mathrm{X}^- + \mathrm{Zn} \xrightarrow[\mathrm{THF,\ r.t.}]{\mathrm{Pd\text{-}cat.}} \mathrm{Ar\text{-}Ar} + 2\mathrm{Ar\text{-}I} + \mathrm{ZnX_2} \qquad (1)$$

A typical procedure is as follows. A mixture of diphenyliodonium bromide (0.72 g, 2 mmol), activated zinc dust (0.13 g, 2 mg-atom), and Pd(acac)$_2$ (30 mg, 0.1 mmol) in dry THF (5 ml) was stirred at room temperature under argon atmosphere. A reaction immediately occured, as indicated by the fast disappearance of crystal of diphenyliodonium bromide and by the exchange of suspended solution color from yellow to pale green. Then, the mixture was filtered and the solvent was evaporated. Distillation of the residue gave iodobenzene (0.33 g, 80% yield), and then recrystallization of the remaining residue from hexane gave biphenyl (mp 69-70°C, 0.14 g, 91% yield).

Various kinds of palladium and nickel compounds were examined as a catalyst in the reaction of diphenyliodonium chloride, and the results were summarized in Table 1. All palladium species were effective for the reaction; especially Pd(acac)$_2$ was the most suitable catalyst. In the absence of a catalyst,the reduction of diphenyliodonium chloride occurred (in this case, benzene and iodobenzene were formed), and the coupling reaction did not.

Among other metals examined as a reductive agent, Sn and Cu were slightly active affording biphenyl in the yield of 16% and 29%, respectively, while Mg was

Table 1. Effect of Catalyst

| Catalyst | Yield (mol%)[a] | |
|---|---|---|
| | Ph-Ph | Ph-I |
| Pd(acac)$_2$ | 96 | 99 |
| Pd(OAc)$_2$ | 62 | 92 |
| PdCl$_2$ | 28 | 85 |
| Pd(PPh$_3$)$_2$Cl$_2$ | 33 | 92 |
| Pd(dba)$_2$ | 36 | 92 |
| NiCl$_2$ | 3 | 93 |
| Ni(PPh$_3$)$_2$Cl$_2$ | 2 | 96 |

a) Yield were determined by GLC.

almost inactive. The reaction, without the aid of zinc, did not occur at all.

A variety of diaryliodonium salts can be used for the reaction as shown in Table 2. In the reaction of substituted diphenyliodonium bromides, the corresponding biaryls were readily and selectively obtained. As compared with the Ullmann reaction, the substituent effect is not remarkably on the present reaction. In particular, dinitrobiphenyl was also obtained in good yield from bis(nitrophenyl)iodonium bromide in the palladium-zinc system, while in the NiCl$_2$-Grignard reagent system bis(nitrophenyl)iodonium bromide failed to react.[4)]

As shown in Eq.1 iodoarene was the another product in the reaction. However, it was easily converted to diaryliodonium salts in sufficient yield as follows.[5)]

$$\text{Ar-I} \xrightarrow[\text{2) Ar-H,}\quad\text{3) X}^-]{\text{1) Oxidizing agent}} [\text{Ar-I}^+\text{-Ar}]\text{X}^- \tag{2}$$

Since the present method is operationally simple, highly selective, and widely applicable, it offers advantages over the previous methods for the preparation of substituted biaryls with either electron-releasing or -withdrawing groups.

Table 2. Reductive Coupling of Diaryliodonium Salts with Pd-Zn System

| Ar$_2$I$^+$X$^-$ | | Time | Yield (mol%)[a] | | Ar$_2$I$^+$X$^-$ | | Time | Yield (mol%)[a] | |
|---|---|---|---|---|---|---|---|---|---|
| Ar | X | (min) | Ar-Ar | Ar-I | Ar | X | (min) | Ar-Ar | Ar-I |
| Ph | Cl | 2 | 96(80) | 99(83) | 4-$^t$Bu | Br | 4 | 98(93) | 100(64) |
| Ph | Br | 3 | 94(91) | 98(80) | 4-MeO | Br | 10 | 88(82) | 92(88) |
| Ph | I | 10 | 50 | 100 | 4-Cl | Br | 3 | 92(90) | 96(83) |
| 4-Me | Br | 3 | 96(91) | 97(78) | 3-NO$_2$ | Br | 30 | 95(91) | 94(90) |

a) Yield were determined by GLC. Parentheses were isolated yields.

## References

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