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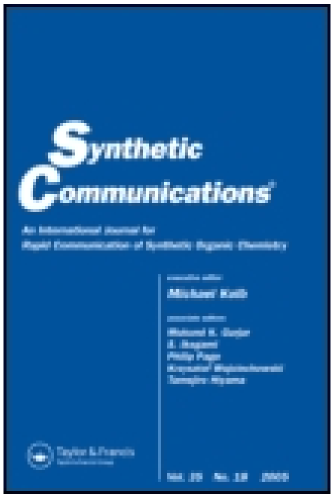

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HYPERVALENT IODINE IN SYNTHESIS. 83. PALLADIUM-CATALYZED CARBONYLATIVE COUPLING OF DIARYLIODONIUM SALTS MEDIATED BY INDIUM

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HYPERVALENT IODINE IN SYNTHESIS. 83. PALLADIUM-CATALYZED CARBONYLATIVE COUPLING OF DIARYLIODONIUM SALTS MEDIATED BY INDIUM

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ABSTRACT

In the presence of palladium catalyst and indium diaryliodonium salt; react with carbon monoxide under mild reaction conditions to give diaryl ketone; in moderate yields.

In the previous paper we have reported catalytic reductive coupling of diaryliodonium salts promoted by palladium–indium system to form biaryls in good yields.[1] We have found that addition of carbon monoxide to the reaction mixture results in the formation of symmetrical ketones. Here we wish to report preliminary results of an investigation on palladium–indium promoted carbonylative coupling of diaryliodonium salts to diaryl ketones.

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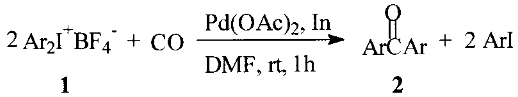


$$\underset{\mathbf{1}}{2\,Ar_2I^+BF_4^-} + CO \xrightarrow[\text{DMF, rt, 1h}]{Pd(OAc)_2,\ In} \underset{\mathbf{2}}{ArC(=O)Ar} + 2\,ArI$$

Scheme 1.

In fact, in the presence of palladium catalyst and indium, simple stirring a solution of diaryliodonium salts in DMF under one atmosphere pressure of carbon monoxide at room temperature gave, after work up and isolation, the diaryl ketone (Sch. 1).

In order to determine the optimum conditions for this reaction, we examined the effects of several factors on the carbonylative coupling of diphenyliodonium tetrafluoroborate. We found that solvent and palladium catalyst have obvious effects on the reaction. Among the selected solvents including DMF, acetone, DME, THF and dioxane, DMF is the best choice. Among the three tested palladium catalysts, $Pd(OAc)_2$ is the most effective. Examination of the reaction of diphenyliodonium tetrafluoroborate showed that except the major product benzophenone, biphenyl was obtained in 13% yield, but benzil was not obtained (Entry 1). This reaction also exhibits a dependence of the anion associated with the iodonium salts (Table 1, Entries 9, 10, 14). In particular, BF_4^- results in higher yields than Cl^-, Br^-, I^-. When we use diaryliodonium halide instead of diaryliodonium tetrafluoroborate, we found that except diaryl ketone, dicarbonylation product was also obtained in 5, 10 and 32% yield respectively (Entries 9, 10, 14). We also found that the reaction could not occur in the absence of indium (Entry 8).

A variety of diaryliodonium salts with various substituents including methyl, chloro, methoxy, nitro and bromo were tested. It was found that all of them can undergo the carbonylative coupling rapidly in the presence of carbon monoxide, $Pd(OAc)_2$ and indium at room temperature. The results are summarized in Table 1. All the products gave satisfactory m.p., IR and ^1H NMR data consistent with literature data.

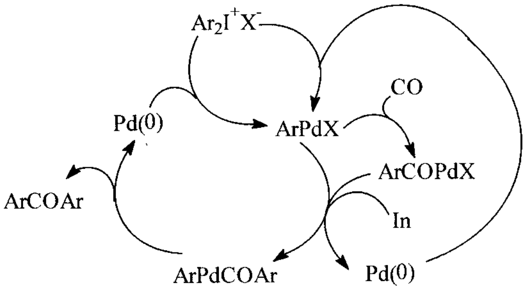
The mechanism of this reaction is not clear at the present stage. However, we consider that Ar-Pd-X and ArCOPdX formed as intermediates act an important role in this reaction. One possible pathway is a reaction of an arylpalladium compound with an acylpalladium compound to via a direct electron transfer from indium to form acylarylpalladium compound which occurs a reductive elimination to afford diaryl ketone. It is shown in Sch. 2.

As shown in Sch. 1, iodoarene was the another product in the reaction. However, it was easily converted to diaryliodonium salts in sufficient yield as described in our previous paper.[1]

Table 1. Carbonylative Coupling of Diaryliodonium Salts with Palladium–Indium System[a]

Entry	$Ar_2I^+BF_4^-$	Solvent	Catalyst	Product	Yield[b] (%)
1	$Ph_2I^+BF_4^-$ **1a**	DMF	$Pd(OAc)_2$	**2a**	71
2	**1a**	Acetone	$Pd(OAc)_2$	**2a**	50
3	**1a**	THF	$Pd(OAc)_2$	**2a**	38
4	**1a**	DME	$Pd(OAc)_2$	**2a**	33
5	**1a**	Dioxane	$Pd(OAc)_2$	**2a**	16
6	**1a**	DMF	$PdCl_2(PPh_3)_2$	**2a**	60
7	**1a**	DMF	$Pd(PPh_3)_4$	**2a**	55
8[c]	**1a**	DMF	$Pd(PPh_3)_4$	**2a**	0
9	$Ph_2I^+Cl^-$ **1a′**	DMF	$Pd(OAc)_2$	**2a**	60
10	$Ph_2I^+Br^-$ **1a″**	DMF	$Pd(OAc)_2$	**2a**	55
11	(p-Tol)$_2I^+BF_4^-$ **1b**	DMF	$Pd(OAc)_2$	**2b**	67
12	(p-$ClC_6H_4)_2I^+BF_4^-$ **1c**	DMF	$Pd(OAc)_2$	**2c**	64
13	(p-$CH_3OC_6H_4)_2I^+$ BF_4^- **1d**	DMF	$Pd(OAc)_2$	**2d**	58
14	(p-$CH_3OC_6H_4)_2I^+$ I^- **1d′**	DMF	$Pd(OAc)_2$	**2d**	25
15	(p-$BrC_6H_4)_2I^+BF_4^-$ **1e**	DMF	$Pd(OAc)_2$	**2e**	57
16	(m-$NO_2C_6H_4)_2I^+BF_4^-$ **1f**	DMF	$Pd(OAc)_2$	**2f**	44

[a]The reaction was carried out under 1 atm. CO atmosphere at room temperature in 5 mL solvent for 1 h in the presence of 1 mmol diaryliodonium salt, 5 mol% palladium catalyst and 0.5 mg-atom indium; [b]Yield of isolated product; [c]Indium was absent, the amount of palladium catalyst was stoichometric.



Scheme 2.

In conclusion, the carbonylative coupling reaction of diaryliodonoum salts can proceed rapidly in the presence of $Pd(OAc)_2$ and indium at room temperature under one atmosphere pressure of carbon monoxide to give symmetrical diaryl ketones in moderate yields. With the advantages of

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simple operation, mild reaction conditions and reasonable yield, it offers a convenient method for the preparation of diaryl ketones. Furthermore, the range of useful application of indium-mediated transformations in organic synthesis has been extended.

EXPERIMENTAL

Melting points were uncorrected. ^{1}H NMR data were recorded on Advance 400 spectrometer using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were determined on Vector 22 infrared spectrometer with KBr pallet.

General Procedure for the Preparation of Diaryl Ketones

A mixture of diaryliodonium salt (**1**) (1 mmol), indium (0.5 mg-atom, cut into small slices), $Pd(OAc)_2$ (5 mol%) and DMF (5 mL) was stirred under carbon monoxide at room temperature for 1 h. The reaction mixture was diluted with saturated NH_4Cl aqueous (20 mL), and extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. After removal of the solvent under vacuum, the residue was chromatographed on silica gel plate using *n*-hexane/ethyl acetate (9 : 1) for **2a–d** and *n*-hexane/ethyl acetate (6 : 1) for **2e**, **2f** as a developer to give pure product (**2**).

Physical and Spectroscopic Data

Benzophenone 2a: M.p. 48–50°C (lit.[2] 49–51°C). ^{1}H NMR δ_H 7.49 (m, 4H), 7.60 (m, 2H), 7.80 (m, 4H). IR ν_{max}/cm^{-1} 3060, 1660, 1599, 1578, 1448, 1318, 1278, 1176, 942, 920, 764, 701, 639.

4,4′-Dimethylbenzophenone 2b: M.p. 92–94°C (lit.[3] 95–95.5°C). ^{1}H NMR δ_H 2.44 (s, 6H), 7.27 (m, 4H), 7.70 (m, 4H). IR ν_{max}/cm^{-1} 1644, 1604, 1509, 1458, 1318, 1257, 1165, 1022, 931, 851, 838, 770.

4,4′-Dichlorobenzophenone 2c: M.p. 146–147°C (lit.[4] 147–148°C). ^{1}H NMR δ_H 7.47 (m, 4H), 7.72 (m, 4H). IR ν_{max}/cm^{-1} 1654, 1588, 1484, 1399, 1308, 1286, 1089, 1014, 929, 852, 832, 754, 669.

4,4′-Dibromobenzophenone 2d: M.p. 174–176°C (lit.[5] 176°C). ^{1}H NMR δ_H 7.65 (s, ArH). IR ν_{max}/cm^{-1} 1643, 1607, 1312, 1278, 1177, 927, 751.

4,4′-Dimethoxybenzophenone 2e: M.p. 142–144°C (lit.[6] 144–145°C). ^{1}H NMR δ_H 3.89 (s, 6H), 6.96 (d, 4H), 7.79 (d, 4H). IR ν_{max}/cm^{-1} 1645, 1584, 1396, 1303, 1289, 1073, 1012, 928, 955, 826, 751, 663.

3,3′-Dinitrobenzophenone 2f: M.p. 150–152°C (lit.[7] 152–153°C). ^{1}H NMR δ_H 7.73 (m, 2H), 8.45 (m, 1H), 8.47 (m, 1H), 8.49 (m, 1H), 8.51 (m, 1H), 8.97 (m, 2H). IR ν_{max}/cm^{-1} 1708, 1618, 1532, 1482, 1418, 1353, 1325, 1303, 1085, 922, 777, 720, 705.

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