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CATALYTIC CARBONYLATION OF DIARYLIODONIUM SALTS PROMOTED BY PALLADIUM-ZINC SYSTEM.
A NEW SYNTHESIS OF DIARYL KETONES AND DIARYL-α-DIKETONES[1)]

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Diaryliodonium salts react with carbon monoxide, in the presence of zinc and a catalytic amount of palladium acetate, to give a mixture of the corresponding diaryl ketones and diaryl-α-diketones under mild conditions.

Extensive studies on the catalytic carbonylation of organic halides with palladium compounds are well known.[2)] Recently, syntheses of α-ketoamides by palladium catalyzed double carbonylation have been reported.[3)] In the previous paper we have reported palladium-base catalyzed carboalkoxylation and amidation of diaryliodonium salts under an atmospheric pressure of carbon monoxide.[4)] Diaryliodonium salts react with palladium-zinc system in the absence of carbon monoxide to form biaryls in excellent yields.[5)] We have found that the addition of carbon monoxide to the reaction mixture results in the formation of symmetrical ketones ArCOAr and ArCOCOAr. In this letter, we wish to report preliminary results of an investigation on palladium-zinc promoted carbonylation of diaryliodonium salt to diaryl ketone and diaryl-α-diketone.

$$2[\mathrm{Ar{-}I^{+}{-}Ar}]\mathrm{X^{-}} + \mathrm{CO} + \mathrm{Zn} \xrightarrow{\mathrm{Pd(OAc)_2}} \mathrm{ArCOAr}\,,\ \mathrm{ArCOCOAr} + 2\mathrm{ArI} + \mathrm{ZnX_2}$$

A typical procedure is as follows. A mixture of diphenyliodonium chloride (0.63 g, 2 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), zinc dust (0.13 g, 2 mg-atom), and acetone (10 ml) was stirred at room temperature for one hour under a carbon monoxide atmosphere. The reaction mixture was analyzed by gas chromatography. Benzophenone and benzil were obtained in good yields as carbonylation products, the latter resulting from a formal double insertion of carbon monoxide. Biphenyl was a by-product of the reaction. The results are shown in Table 1.

Diaryl ketone and diaryl-α-diketone are produced in this reaction in various solvents (Runs 1-5), but methyl benzoate is also formed in methyl alcohol. Zinc was most effective as a reducing metal, use of other metals such as Cu and Sn results in lower yields of ketones (Runs 7 and 8). In the absence of zinc, the reaction did not proceed at all. To achieve a catalytic reaction with palladium, a stoichiometric amount of zinc is required. Diaryl-α-diketone appears to be formed in preference of diaryl ketone at high pressures of carbon monoxide (Runs 9 and 10). A variety of diaryliodonium salts can be used for the reaction, the

Table 1. Carbonylation of Diaryliodonium Salts with Palladium-Zinc System[a)]

Run	$[Ar\text{-}\overset{+}{I}\text{-}Ar]X^-$		CO	Metal	Solvent[b)]	Products Yield (mol%)[c)]			
	Ar	X	(atom)			ArCOAr	ArCOCOAr	ArAr	ArI
1	Ph	Cl	1	Zn	AC	56	24	18	96
2	Ph	Cl	1	Zn	DME	47	13	22	98
3	Ph	Cl	1	Zn	DMF	55	8	34	92
4	Ph	Cl	1	Zn	$MeNO_2$	60	8	30	93
5[d)]	Ph	Cl	1	Zn	MeOH	32	5	37	98
6[e)]	Ph	Cl	1	Zn	AC	60	21	18	97
7[f)]	Ph	Cl	1	Cu	AC	31	17	16	95
8	Ph	Cl	1	Sn	AC	42	4	7	100
9	Ph	Cl	10	Zn	AC	42	40	13	91
10	Ph	Cl	30	Zn	AC	31	45	18	95
11	Ph	Br	1	Zn	AC	61	16	23	92
12	$4\text{-}Me\text{-}C_6H_4$	Br	1	Zn	AC	52	11	22	98
13	$4\text{-}{}^tBu\text{-}C_6H_4$	Br	1	Zn	AC	59	14	19	90
14	$4\text{-}Cl\text{-}C_6H_4$	Br	1	Zn	AC	45	16	28	94
15	$4\text{-}Br\text{-}C_6H_4$	Br	1	Zn	AC	51	13	27	97

a) A mixture of diaryliodonium salt (2 mmol), $Pd(OAc)_2$ (0.1 mmol), metal (2 mg-atom), and solvent (10 ml) was stirred for 1 h at room temperature.

b) AC: Acetone, DME: 1,2-Dimethoxyethane, DMF: N,N-Dimethylformamide.

c) Based on diaryliodonium salt used. Determined by GLC.

d) Products also contained a 26% of PhCOOMe. e) Zinc (1 mg-atom) was used.

f) Products also contained a 30% of PhCl.

corresponding diaryl ketones and diaryl-α-diketones were readily obtained (Runs 11-15). Thus, palladium-zinc promoted carbonylation of diaryliodonium salts is applicable to the synthesis of various aryl ketones.

The mechanism of this novel route for aryl ketones is not clear at the present stage. However, we consider that Ar-Pd-X and ArCO-Pd-X 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 form diaryl ketone and coupling of two acylpalladium compounds to afford diaryl-α-diketone.

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