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Synthesis of Aryl Esters by Pd-catalysed Carbonylation of Aryl Iodides

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Carbonylation of aryl iodides in the presence of phenols leading to $ArCO_2Ar'$ has been carried out.

Carbonylation of aryl iodides catalysed by palladium complexes in the presence of water, alcohols or amines provides a convenient method[1] for the synthesis of various carbonyl compounds such as arenecarboxylic acids and their derivatives.[2–8]

Carbonylation of aryl halides in the presence of phenols as nucleophilic reagents has not been satisfactorily described in the literature and there are reasonable doubts about the possibility of such a reaction, in spite of the fact that it seems very attractive. Phenol esters are used in the capacity of liquid crystals[9] and biologically active compounds.[10] Several methods are available to obtain phenol esters, based on the acylation of arenes by chloroformates,[11] of phenols by anhydrides and acyl chlorides[9,12] or by acids themselves in the presence of dicyclohexylcarbodiimide.[10] The main drawbacks of the acylation techniques are the harsh conditions,[9,11,12] low yields[10,11] and the necessity of using the corresponding acids.

By studying the carbonylation of ArI to form methyl esters of aromatic acids we have shown that high yields can be achieved by using a palladium catalyst without phosphine ligands [for

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Table 1 Carbonylation of aryl iodides effected by ROH and bases (1 atm CO, 60 °C)

Entry	Ar in ArI	R in ROH	Base	Mol. ratio ArI:ROH:B	Solvent	Cat., mol%[a]	Time/h	Conversion (%)	Yield (%)[b] $ArCO_2H$	Yield (%)[b] $ArCO_2R$
1	p-$NO_2C_6H_4$	Me	NaOH	1:60:1,5	MeOH	B,0.5	1	99	10	82
2	„	p-Tol	NaOH	1:1.25:1.2	Dioxane	„	6	88	14	70
3	„	„	TolONa	1:0:1.1	„	„	2.3	58	4	50
4	„	„	NaOH	1:1.25:1	DMF	„	3	94	15	78
5	„	„	„	1:1.25:1.2	„	C,0.5	4	35	20	12
6	„	„	K_2CO_3	1:1.25:1	„	B,0.5	6	80	13	67
7	„	„	Et_3N	1:1,2:1.6	„	„	5	44	2	40
8	Ph	Ph	NaOH	1:1.2:1.4	„	B,1	5	64	–	62
9	„	„	Et_3N	1:1.2:2	„	B,0.5	60	80	2	72
10	„	„	PhONa	1:0:1.2	„	„	5	99	0	99

[a] B = $Pd(OAc)_2$, C = $PdCl_2(PPh_3)_2$. [b] Yields determined by TLC and UV spectroscopy.

example, $Pd(OAc)_2$ as a precursor of the catalyst] and NaOH as base in methanol [eqn. (1)].

$$p\text{-}NO_2C_6H_4I + MeOH + NaOH \xrightarrow{Pd(OAc)_2} p\text{-}NO_2C_6H_4CO_2Me \quad (1)$$

Under these conditions the yield of ester p-$NO_2C_6H_4CO_2Me$ is 82% and 10% of p-$NO_2C_6H_4CO_2H$ is formed. The formation of acid as a by-product may result from the hydrolysis [eqn. (2)] of the ester in the presence of NaOH or from hydroxycarbonylation [eqn. (3)] proceeding along with the alkoxycarbonylation.

$$p\text{-}NO_2C_6H_4CO_2Me + NaOH \longrightarrow p\text{-}NO_2C_6H_4CONa + MeOH \quad (2)$$

$$p\text{-}NO_2C_6H_4I + CO + 2NaOH \xrightarrow{Pd(OAc)_2} p\text{-}NO_2C_6H_4CO_2Na + H_2O + NaI \quad (3)$$

We have studied two carbonylation reactions: the reaction of PhI in the presence of PhOH and the reaction of p-$NO_2C_6H_4I$ in the presence of p-TolOH (Table 1) under varying conditions and have shown that phenol esters $ArCO_2Ar'$ can be obtained in high yields (entries 4, 9, 10). The presence of phosphine ligands retards the reaction (Table 1, entry 5).

A certain amount of acid $ArCO_2H$ is formed along with ester $ArCO_2Ar'$ in the presence of NaOH in *N,N'*-dimethylformamide (DMF) (Table 1, entries 4, 6, 7), and this increases in the presence of electron-withdrawing substituents in the Ar and Ar'moieties. Hence, the following hydrolysis takes place. Using Et_3N as a base (Table 1, entries 7, 9) in the absence of OH^- or H_2O we can avoid the formation of acid, but the rate of reaction is very small in this case. Reaction (4) proceeds very rapidly and selectively when we use sodium phenolates as nucleophile agents (Table 1, entries 3, 10), but this method requires an additional stage.

$$ArI + CO + Ar'ONa \xrightarrow{\text{'Pd'}} ArCO_2Ar' \quad (4)$$

Ar = Ph, p-$NO_2C_6H_4$; Ar' = Ph, p-Tol

Thus, carbonylation of ArI in the presence of 0.5 mol% $Pd(OAc)_2$, NaOH and a small excess of phenol at 1 atm CO in DMF can be considered as the optimum conditions for obtaining $ArCO_2Ar'$ [eqn. (5)]. The excess of phenol and the small amount of $ArCO_2H$ can easily be removed using aqueous NaOH.

Table 2 Synthesis of aryl esters $ArCO_2Ar'$ *via* palladium-catalysed carbonylation of aryl iodides ArI effected by Ar'OH and NaOH (1 atm CO, 60 °C, DMF, 0.5 mol% $Pd(OAc)_2$ 1–1.5 mol NaOH per mol ArI)

Entry	Ar in ArI	Ar in Ar'OH	Time/h	Product	Yield(%)[a]
1	p-$NO_2C_6H_4$	p-MeC_6H_4	3	p-$NO_2C_6H_4CO_2C_6H_4Me$-p	78(76)
2	„	p-BrC_6H_4	2	p-$NO_2C_6H_4CO_2C_6H_4Br$-p	43[b](35)
				p-$NO_2C_6H_4CO_2H$	30
3	„	p-IC_6H_4	2.5	p-$NO_2C_6H_4CO_2C_6H_4I$-p	(50)
4	C_6H_4	Ph[c]	5	$PhCO_2Ph$	99(89)
5	„	o-$NO_2C_6H_4$	10	$PhCO_2H$	94
				$PhCO_2C_6H_4NO_2$-o	0
6	„	m-$NO_2C_6H_4$	5	$PhCO_2C_6H_4NO_2$-m	(63)
7	p-MeC_6H_4	p-$NO_2C_6H_4$	4	p-$MeC_6H_4CO_2C_6H_4NO_2$-p	88(61)
8	Ph	o-$MeOC_6H_4$	6	$PhCO_2C_6H_4OMe$-p	(97)
9	o-MeC_6H_4	Ph	1.5	o-$MeC_6H_4CO_2Ph$	(81)
10	p-$MeOC_6H_4$	p-MeC_6H_4	6	p-$MeOC_6H_4CO_2C_6H_4Me$-p	80(78)
11	„	p-BrC_6H_4	4.7	p-$MeOC_6H_4CO_2C_6H_4Br$-p	(62)
12	β-Naphthyl	Ph	1	2-$C_{10}H_7CO_2Ph$	(85)
13	p-ClC_6H_4	p-BrC_6H_4	8	p-$ClC_6H_4CO_2C_6H_4Br$-p	76(75)
14	p-IC_6H_4	p-ClC_6H_4	20	(p-$ClC_6H_4OCO)_2C_6H_4$-p	(35)
15	p-$HOCC_6H_4$	Ph	3.5	p-$HOCC_6H_4CO_2Ph$	48
16	p-$MeOC_6H_4$	p-HOC_6H_4	8	(p-$MeOC_6H_4CO_2)_2C_6H_4$-p	(76)
17	p-ClC_6H_4	p-HOC_6H_4	12	(p-$ClC_6H_4CO_2)_2C_6H_4$-p	32(31)
18	α-Py	Ph	4	2-$C_5H_4CO_2Ph$	0[d]
19	α-Py	Ph	4	2-$C_{10}H_7CO_2Ph$	8[e]
	β-Naphth	„	„	2-$C_{10}H_7CO_2H$	11

[a] Yields determined by TLC and UV spectroscopy, isolated yields in parentheses. [b] 18% of $NO_2C_6H_4I$ recovered. [c] Neat PhONa as base. [d] 95% of α-C_5H_4NI. [e] 77% of 2-$C_{10}H_7I$.

$$ArI + CO + Ar'OH \xrightarrow{1\ atm.\ CO,\ 60°C,\ DMF} ArCO_2Ar' \quad (5)$$

The yields of reaction (5) vary from moderate to high (Table 2). A decrease in the yield is observed in the presence of electron-withdrawing substituents in both aryl groups (Table 2, entry 2). the yields remain high, however, if an electron-withdrawing substituent is present in one aryl fragment only (entries 1, 7). $PhCO_2H$ is the sole product in the reaction of PhI with o-$NO_2C_6H_4OH$ (entry 5). The acid is apparently formed in a hydroxycarbonylation process [eqn.(3)] since ester formation [eqn.(5)] would be suppressed due to the low nucleophilicity of o-$NO_2C_6H_4O^-$.

α-Iodopyridine cannot be subjected to carbonylation and hinders the carbonylation of other substrates, for example, 2-iodonaphthalene (Table 2, entry 19). This means that the intermediate complex $PyPdIL_2$ is inert in the carbonylation process, possibly due to the formation of a small amount of bipyridyl ($L_2 = py_2$).

It is also possible to introduce into the carbonylation reaction diiodoarenes and dihydroxyarenes to obtain the corresponding diesters (Table 2, entries 14, 16, 17) [eqns. (6) and (7)].

Electron-withdrawing substituents such as chlorine make the hydroxycarbonylation product essential. A typical experimental procedure was as follows for the synthesis of 2-naphthoic acid phenyl ester. A two-necked flask, thermostated at 60 °C and equipped with a magnetic stirrer and carbon monoxide inlet, was charged with 9 ml of DMF, 1.016 g (4 mmol) 2-iodonaphthalene, 0.46 g (5 mmol) PhOH and 0.3 g (7.5 mmol) NaOH. The mixture was stirred in CO atmosphere for 0.5 h and 0.0044 g of $Pd(OAc)_2$ was added. After 1 h the overall CO consumption reached 97 ml (750 mmHg, 25 °C). The slurry was admixed with 50 ml of water and extracted with benzene (4 × 20 ml). The combined benzene layers were washed with 1 mol dm^{-3} aqueous NaOH (5 × 10 ml) and water, filtered, dried over $MgSO_4$ and evaporated at reduced pressure to give 0.84 g of β-$C_{10}H_7CO_2Ph$ (yield 85%), m.p. 96 °C.

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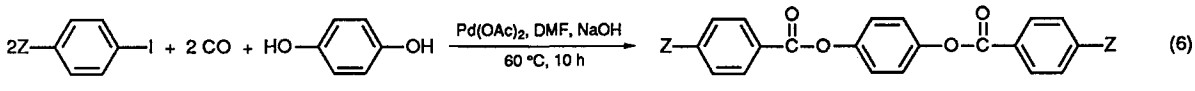
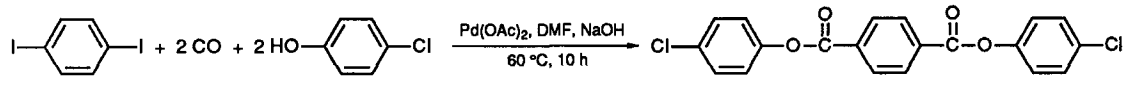


(6)

Z = Cl (31%), Z = MeO (76%)



(35%) (7)