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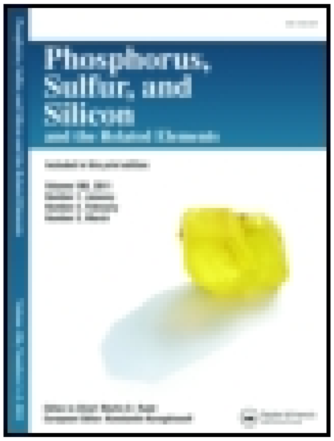

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Mw-Assisted P-C coupling reaction using P-ligand-free $Pd(oAc)_2$ catalyst

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MW-ASSISTED P-C COUPLING REACTION USING P-LIGAND-FREE Pd(OAc)$_2$ CATALYST

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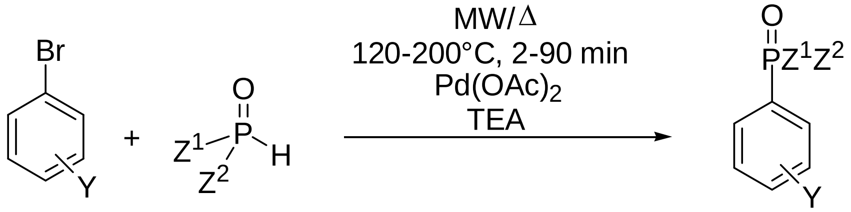
Abstract *P-C coupling reactions of a variety of >P(O)H species with aryl bromides were found to take place under P-ligand-free microwave conditions.*



Y= H, 4-MeO, 3-MeO, 4-^{t}Bu, 4-Pr, 4-Et, 4-Me, 3-Me, 4-F, 3-F, 4-Cl, 3-Cl, 4-CO$_2$Et, 3-CO$_2$Et, 4-C(O)Me, 3-C(O)Me

Z^1	OR	Ph	R	Ph
Z^2	OR	OR	R	Ph

R = Et, Pr, ^{i}Pr, Bu, ^{i}Bu, ^{i}Pent, Bn

Keywords Microwave; P-C coupling; arylphosphonates; diphenylphosphinates; phosphine oxides

Nowadays, the P-C coupling reaction is in the focus. In general, the P-C coupling reaction was carried out in the presence of $Pd(PPh_3)_4$ as the catalyst using triethylamine or other bases in toluene.[1,2] Many alternative approaches (other catalysts, microwave(MW)-assisted and phase transfer-catalyzed accomplishments) were described in the last three decades [2,3] We tried to elaborate a new *P*-ligand-free P-C coupling for the synthesis of dialkyl arylphosphonates, alkyl diphenylphosphinates and tertiary phosphine oxides.[5,6] In our experiments different >P(O)H species were reacted with aryl bromides using $Pd(OAc)_2$ as the catalyst and triethylamine as the base, in almost all cases, under solvent-free MW conditions.

The first model reaction was the coupling of diethyl phosphite with bromobenzene (Scheme 1), and the coupling reaction was efficient at 120 °C after 0.5 h and 150 °C after 5 min using 5% $Pd(OAc)_2$ (Table 1/ Entries 1 and 2). Dibutyl phosphite was less reactive, and conversions of 94% and 91% could be attained after prolonged reaction times (Table 1/ Entry 3 and 4). The P-C coupling reactions were also tested under conventional heating. Comparative thermal experiments were not so efficient and they required longer reaction times to achieve good conversions.

Then, the reactions of diethyl phosphite with 4- and 3-substituted aryl bromides were also investigated (Scheme 2). In all cases, the transformations required more forcing conditions (higher temperature, longer reaction time, using a larger amount of $Pd(OAc)_2$) (Table 2).

It was found that both the electron-donating and the electron-withdrawing substituents in positions 4 and 3 decrease the reactivity of aryl bromides. 3-Bromotoluene and 4-fluorobromobenzene were somewhat more reactive than the other aryl derivatives, and the corresponding diethyl arylphosphonates (**2**) were formed in both cases in a yield of 91% at 175 °C in the presence of 5% $Pd(OAc)_2$ (Table 2/ Entries 8 and 11).

Finally, we studied the P–C couplings of phenyl-*H*-phosphinates with bromobenzene, and the corresponding products (**3**) were obtained in acceptable yields (68-92%) using 5% $Pd(OAc)_2$ at 150 °C for 5 min (Scheme 3). The coupling reaction of diphenylphosphine oxide with aryl bromides, such as bromobenzene, bromotoluene, 4-chlorobromobenzene and 4-fluorobromobenzene, was efficient in the presence of 5% $Pd(OAc)_2$ at 150°C after 5 min and triarylphosphine oxides (**3**) were formed in high yields (83-90%) (Scheme 3). Furthermore, we found that the reaction of dialkylphosphine oxides with bromobenzene gave the corresponding products (**3**) in yield of 80-95% at 175 °C after 1.5 h in acetonitrile (Scheme 3). In this case, the use of solvent was necessary to avoid decomposition.

It was found that diphenylphosphine oxide have higher reactivity than dialkyl phosphite and alkyl phenyl-*H*-phosphinates.

In conclusion, the *P*-ligand-free Hirao reaction has been elaborated by us for the P-C coupling of different aryl bromides and a wide range of >P(O)H species, such as dialkyl phosphite, phenyl-*H*-phosphinates and secondary phosphine oxides. In most of the cases, the corresponding products were formed in high yields (73-93%). We showed that the novel method is of general value and it is an environmentally friendly approach for the P-C coupling reactions.

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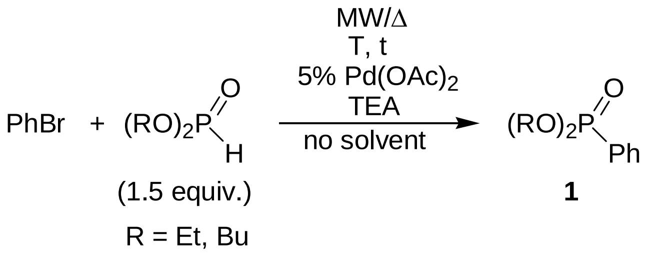

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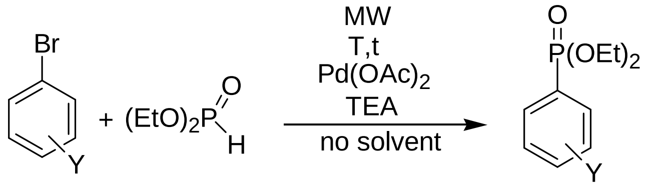
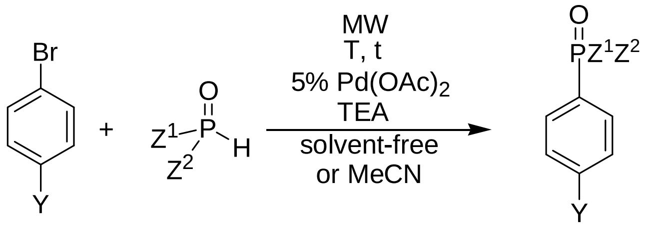
Scheme 1



2

Y= 4-MeO, 3-MeO, 4-^{t}Bu, 4-Pr, 4-Et, 4-Me, 3-Me, 4-Cl, 3-Cl, 4-F, 3-F, 4-CO_2Et, 3-CO_2Et, 4-C(O)Me, 3-C(O)Me

Scheme 2



Y = H, Me, Cl, F

3 (68-95%)

Z^1	OEt	OPr	O^{i}Pr	OBu	O^{i}Bu	O^{i}Pent	Ph	Pr	Bu	Bn
Z^2	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Pr	Bu	Bn

Scheme 3

Table 1 P-C coupling of dialkyl phosphite with bromobenzene under MW conditions

R	**T** **[°C]**	**t** **[min]**	**Conversion**[a,b] **[%]**	**Yield** **[%]**	**Entry**
Et	120	30	97	90	1
Et	150	5	99	93	2
Bu	120	90	94	84	3
Bu	150	20	91	77	4

[a] On the basis of GC analysis. [b] Average from 3 parallel reactions.

Table 2 The coupling reaction of aryl bromides with diethyl phosphite

Y	$Pd(OAc)_2$ [%]	T [°C]	t [min]	Conversion[a] [%]	Yield [%]	Entry
H	5	150	5	99	93	1
4-MeO[b]	5	200	2	80[c]	69	2
3-MeO[b]	10	200	2	93[c]	79	3
4-^{t}Bu	10	200	2	68[c]	60	4
4-Pr	10	200	2	86[c]	71	5
4-Et	10	175	15	93[c]	85	6
4-Me	10	175	10	86[c]	73	7
3-Me	5	175	10	100	91	8
4-Cl	10	200	2	100	83	9
3-Cl	10	175	10	95	87	10
4-F	5	175	5	99	91	11
3-F	10	175	5	100	88	12
4-CO_2Et	5	175	15	100	89	13
3-CO_2Et	10	200	2	93	81	14
4-C(O)Me	5	175	15	100	71	15
3-C(O)Me	10	175	5	100	92	16

[a] On the basis of GC analysis. [b] In the presence of 3 equiv. of diethyl phosphite. [c] No change on the further irradiation.