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Liancheng Yang^a; Longhe Xu^a; Zaizhou Tao^b

^a State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China ^b Shenyang Research Institute of Chemical Industry, Shenyang, China

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Palladium-Catalyzed Arylation of 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with Halogen-Substituted Phenols

Liancheng Yang,¹ Longhe Xu,¹ and Zaizhou Tao²

¹State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China

²Shenyang Research Institute of Chemical Industry, Shenyang, China

Phenol functionalized 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives are synthesized via palladium-catalyzed arylation of DOPO with halogen-substituted phenols. 2-, 3-, and 4-Substituted halogen phenols are successfully applied to the cross-coupling reactions. This method is mild, convenient, and leads to high yields (65–95%).

Keywords Arylation; catalysis; cross-coupling; DOPO; palladium

INTRODUCTION

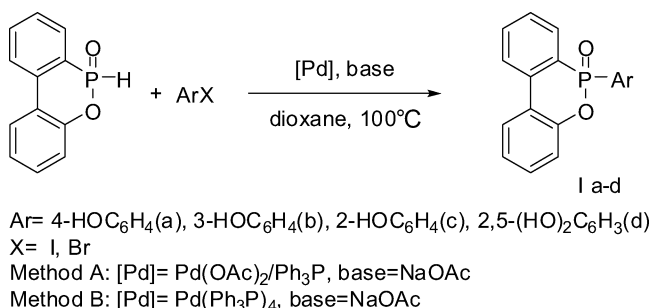
The cyclic organic phosphorus compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), has received notable attention in research due to its attractive properties.^{1–5} DOPO derivatives have been widely incorporated into polymers for improving their flame retardant properties and thermal stability.^{6–13} For example, an aromatic DOPO derivative containing a phenol functional group, 2-(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (ODOPB), has been used as a reactive flame retardant.^{14–18} Owing to the high content of phosphorus and of aromatic groups, ODOPB exhibited not only better flame retardant properties but also higher thermal stability and glass transition temperature.¹⁴ Moreover, incorporation of ODOPB into the molecular structure of polymers via phenol groups brought improved organosolubility to the polymer, and avoided the molecular migration of flame retardants.¹⁵ However, to the best of our

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Address correspondence to Liancheng Yang, Liaoning Petrochemical Vocational Technology College, Room 213, Petrochemical Department, Jinzhou 121001, China. E-mail: ylc94@163.com

knowledge, only three phenol derivatives of DOPO have been reported; they were synthesized by the addition of DOPO to quinones.^{19–21} In the present work, we attempt to synthesize phenol functionalized DOPO derivatives through palladium-catalyzed phosphorus–carbon formation reactions. Although cross-coupling of P–H compounds with aryl halides, catalyzed by transition metal catalyst (such as Pd, Ni, Cu), have been studied in sufficient detail during the last two decades,^{22–32} far from all the reported procedures are able to be used in the arylation of DOPO with aryl halides. In particular, triethylamine, which is usually used as a base in such transformations, turned out to be insufficiently effective. Although Beletskaya et al.³³ examined the palladium-catalyzed arylation reactions of DOPO with some aryl iodides and aryl bromides, no halogen-substituted phenols were used as coupling partners. In this article, we wish to report a general procedure for palladium-catalyzed arylation of DOPO with halogen-substituted phenols.



SCHEME 1

RESULTS AND DISCUSSION

The arylation conditions were optimized using the reactions of DOPO with 4-iodophenol as examples (Scheme 1). The natures of the base, solvent, and catalyst were varied. The reaction conditions and the yields of P-phenyl derivative are summarized in Table I. Firstly, PdCl₂(Ph₃P)₂, an effective catalyst in the palladium catalyzed arylation of DOPO,³³ was used as a catalyst. Various bases were added to the reaction mixture, and the reaction was carried out in dioxane at reflux temperature. Low to good yields of the target products were obtained (entries 2–9) except entry 6, in which the reaction mainly produced byproducts probably caused by the addition of P–H to propylene oxide. The best result

TABLE I Cross Coupling of DOPO with 4-Iodophenol (Ia)^a

Entry	Base	Catalyst (5% mol) + Ligand (10% mol)	Phase-transfer catalyst (20%mol)	Reaction time, h	Yield, ^b % ^b
1	Et ₃ N	—	—	24	No reaction
2	Et ₃ N	PdCl ₂ (Ph ₃ P) ₂	—	24	8
3	Et ₃ N	PdCl ₂ (Ph ₃ P) ₂	BTEAC	24	10
4	<i>i</i> -Pr ₂ NEt ^c	PdCl ₂ (Ph ₃ P) ₂	BTEAC	24	12
5	Cy ₂ NMe ^c	PdCl ₂ (Ph ₃ P) ₂	BTEAC	24	45
6	Propylene oxide	PdCl ₂ (Ph ₃ P) ₂	BTEAC	24	—
7	K ₂ CO ₃	PdCl ₂ (Ph ₃ P) ₂	BTEAC	24	58
8	NaOAc	PdCl ₂ (Ph ₃ P) ₂	—	4	67
9	NaOAc	PdCl ₂ (Ph ₃ P) ₂	BTEAC	4	66
10	NaOAc	Pd(OAc)₂+Ph₃P	—	4	94
11	Et ₃ N	Pd(OAc) ₂ +Ph ₃ P	—	4	83
12	NaOAc	Pd(Ph₃P)₄	—	4	95
13	NaOAc	Pd(Ph ₃ P) ₄	—	5	94 ^d
14	Et ₃ N	Pd(Ph ₃ P) ₄	—	4	85
15	Et ₃ N	PdCl ₂ +Ph ₃ P	—	4	72

^aThe reactions were carried out using DOPO (1 mmol), 4-iodophenol (1 mmol), and base (2 mmol), in dioxane (3 mL) at 100°C under nitrogen atmosphere.

^bIsolated yield.

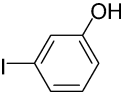

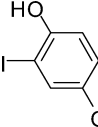
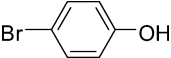
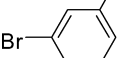
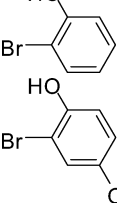
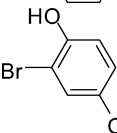
^c*i*-Pr₂NEt: N,N-diisopropylethylamine; Cy₂NMe: N,N-dicyclohexylmethylamine.

^dCH₃CN (3 mL) was used as the solvent and the reaction was carried out at reflux temperature.

was obtained using NaOAc as a base (entry 8). The addition of phase-transfer catalyst (BTEAC) had little effect on the reaction when NaOAc was used as the base (entries 8 and 9). Moreover, the reaction did not proceed in the absence of the catalyst (entry 1). Then, effects of other catalysis system on the cross-coupling reaction were evaluated. It was found that Pd(OAc)₂/Ph₃P, Pd(Ph₃P)₄, and PdCl₂/Ph₃P could catalyze the reaction; however, Pd(OAc)₂/Ph₃P and Pd(Ph₃P)₄ were more effective (entries 10–14). The best procedure for the synthesis of **Ia** was cross coupling of DOPO with 4-iodophenol in the presence of 2 equiv of NaOAc, 5% mol of Pd(OAc)₂, and 10% mol of Ph₃P (method A) [or 5% mol of Pd(Ph₃P)₄ (method B)], which takes 4 h in boiling dioxane (entries 10 and 12). A similar result was obtained when CH₃CN was used as a solvent, and the reaction was completed at 80°C after 5 h (entry 13).

The two methods were then extended to the synthesis of other phenol functionalized DOPO derivatives **Ib–d** (Table II). When iodo-substituted phenols were applied, compounds **Ib–d** were obtained in

TABLE II Cross Coupling of DOPO with Various Halogen-Substituted Phenols^a

Entry	Halogen-substituted phenols	Product	Reaction time, h	Yield, % ^b	Method ^c
1		Ib	4	94	A
2		Ic	4	93	B
3			24	10	A
4		Id	4	78	B
5			12	13	A
6		Ia	12	65	B
7			24	33	B
8		Ib	24	28	B
9					
10		Ic	24	5	B
		Id	24	25	B

^aThe reactions were carried out using DOPO (1 mmol), halogen-substituted phenol (1 mmol), and NaOAc (2 mmol), in dioxane (3 mL) at 100°C under nitrogen atmosphere.

^bIsolated yield.

^cMethod A: Pd(OAc)₂ (5% mol), Ph₃P (10% mol) were used as catalysts. Method B: Pd(Ph₃P)₄ was used as a catalyst.

good to high yields after workup and chromatography on silica gel (eluent 2:98 to 5:95 MeOH/CH₂Cl₂). Compared with method B, method A led to lower yields of **Ic** and **Id** (Entries 3 and 5). This indicated that a steric hindrance effect played an important role using a 2-substituted phenol as coupling partner when Pd(OAc)₂/Ph₃P was used as catalyst. However, the yields of **Ic** and **Id** were greatly improved when Pd(Ph₃P)₄ was applied as the catalyst. As to bromo-substituted phenols, low to

moderate yields of **Ib–d** were obtained (entries 7–10). Extending the reaction times only caused the formation of a considerable amount (more than 50%) of unidentified byproducts.

EXPERIMENTAL

General

DOPO (BMD Chemical Co., Ltd., Shenyang, China) was purified by recrystallization from THF. 2-, 3-, and 4-Iodo (or bromo) phenols were of commercial quality (Aldrich) and used without further purification. 2-Iodobenzene-1,4-diol³⁴ and 2-bromobenzene-1,4-diol³⁵ were prepared according to the reported procedures. Other reagents and solvents were commercially available and distilled, recrystallized, or dehydrated thoroughly. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ¹H NMR spectra were performed on a Mercury 300 spectrometer (Varian, ¹H: 300 MHz) with DMSO-*d*₆ as the solvent and TMS as the internal standard. ³¹P NMR spectra were obtained on the Mercury 300 (Varian, 121 MHz) spectrometer using H₃PO₄ as an internal standard. Infrared spectra were recorded with a PE-983G instrument (Perkin-Elmer). Combustion analyses for C and H elemental composition were made with a Vario EL III analyzer (Elementar). Phosphorus content was determined by oxygen flask method. All reactions were monitored by TLC.

General Procedure for the Arylation of DOPO with Halogen-Substituted Pphenols

Method A

In a flask containing DOPO (216 mg, 1.0 mmol), palladium acetate (11 mg, 0.05 mmol, 0.05 eq), Ph₃P (26 mg, 0.1 mmol, 0.1 eq), NaOAc (164 mg, 2.0 mmol), and halogen-substituted phenol (1.0 mmol) under N₂ were added under stirring dry dioxane (3 mL) at room temperature. The reaction mixture was heated at 100°C until complete consumption of the phenol, which was monitored by TLC. After cooling, the reaction mixture was diluted with ethyl acetate (20 mL), and diluted HCl (1:2, 10 mL) was added, the mixture was stirred, and the aqueous phase was separated and extracted with ethyl acetate (3 × 20 mL). The extracts were combined with the organic phase, then washed with water (3 × 10 mL) and brine (10 mL), and dried over Na₂SO₄. The crude solution is concentrated under reduced pressure, affording a solid purified by column chromatography over silica gel (eluent 2:98 to 5:95 MeOH/CH₂Cl₂).

Method B

Method B was performed the same as method A, except that $\text{Pd}(\text{Ph}_3\text{P})_4$ was used as a catalyst.

4-(6-Oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)phenol (1a)

White solid: mp 256–258°C, IR (KBr): 3451 (Ph-OH); 1600, 1583 (Ph); 1202 (P = O); 1147, 931 (P-O-Ph) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 6.87 (dd, J = 9.0, 3.6 Hz, 2H, ArH), 7.23–7.34 (m, 2H, ArH), 7.41–7.57 (m, 5H, ArH), 7.71–7.76 (m, 1H, ArH), 8.15–8.22 (m, 2H, ArH), 10.26 (s, 1H, OH); ^{31}P NMR (121 MHz, $\text{DMSO}-d_6$, H_3PO_4): δ 24.18. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{O}_3\text{P}$: C, 70.13; H, 4.25; P, 10.05; found: C, 70.20; H, 4.22; P, 10.13.

3-(6-Oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)phenol (1b)

White solid: mp 235–236°C, IR (KBr): 3415 (Ph-OH); 1597 (Ph); 1189 (P = O); 1148, 922 (P-O-Ph) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 6.96–7.08 (m, 2H, ArH), 7.14–7.29 (m, 4H, ArH), 7.37–7.56 (m, 3H, ArH), 7.70 (t, J = 7.2, 1H, ArH), 8.07–8.15 (m, 2H, ArH), 9.62 (s, 1H, OH); ^{31}P NMR (121 MHz, $\text{DMSO}-d_6$, H_3PO_4): δ 23.40. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{O}_3\text{P}$: C, 70.13; H, 4.25; P, 10.05; found: C, 70.18; H, 4.27; P, 10.08.

2-(6-Oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)phenol (1c)

White solid: mp 285–287°C, IR (KBr): 3441 (Ph-OH); 1594 (Ph); 1193 (P = O); 1150, 922 (P-O-Ph) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 6.78–6.83 (m, 1H, ArH), 6.93–6.96 (m, 1H, ArH), 7.22–7.31 (m, 2H, ArH), 7.40–7.61 (m, 4H, ArH), 7.70–7.75 (m, 2H, ArH), 8.17–8.23 (m, 2H, ArH), 10.12 (s, 1H, OH); ^{31}P NMR (121 MHz, $\text{DMSO}-d_6$, H_3PO_4): δ 25.22. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{O}_3\text{P}$: C, 70.13; H, 4.25; P, 10.05; found: C, 70.19; H, 4.22; P, 10.15.

2-(6-Oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)-1,4-dihydroxy Phenylene (1d)

White solid: mp 254–255°C, IR (KBr): 3175 (Ph-OH); 1593, 1502 (Ph); 1473 (P-Ph); 1182 (P = O); 932 (P-O-Ph) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 6.63–6.67 (t, 1H, ArH), 6.89–6.92 (d, 1H, ArH), 7.19–7.32 (m, 2H, ArH), 7.43–7.59 (m, 3H, ArH), 7.62–7.75 (t, 1H, ArH), 8.23–8.24 (d, 2H, ArH), 9.19 (s, 1H, OH), 9.48 (s, 1H, OH); ^{31}P NMR (121 MHz, $\text{DMSO}-d_6$, H_3PO_4): δ 21.92. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{O}_4\text{P}$: C, 66.67; H, 4.04; P, 9.55; found: C, 66.47; H, 4.12; P, 9.31.

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