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Citation:

Scope and Limitations of the Palladium-Catalyzed Cross-Coupling Reaction of in situ Generated Organoboranes with Aryl and Vinyl Halides Shawn P. Maddaford and Brian A. Keay pp 6501 – 6503.

Abstract:

Summary: The in situ palladium(0)-catalyzed Suzuki reaction is shown to be an efficient method for the cross-coupling of aryl-, furyl-, primary, and benzylic boranes with aryl or vinyl bromides and iodides without the isolation of the organoboronic acid or the addition of any external base.

Tables:

Table 1. Various Attempts To Optimize the Yield of Biphenyl via the in Situ Suzuki Cross-Coupling Reaction

solvent	PhX	water or base	catalyst	time (h)	yields of biphenyl (%)
DME	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	20	68
DME	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	2	53
benzene	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	16	61°
benzene	I	H_2O	Pd(PPh ₃) ₄	16	51 ^d
benzene	I	Na ₂ CO ₂	Pd(OAc) ₂ (PPh ₂) ₂	20	85
NMP	$_{\rm Br}$	H ₂ O	$Pd(PPh_3)_4$	17	63
DME	Br	H ₂ O	Pd(PPh ₃) ₄	1.5	62
DME	Br	H ₂ O/TMEDA*	Pd(PPh ₃) ₄	1.5	59
DME	Br		Pd(OAc) ₂ (PPh ₃) ₂	2	76
DME	Br	Na ₂ CO ₃	Pd(PPh ₃) ₄	2	49
DME	$_{\rm Br}$	Na_2CO_3	Pd(Pfuryl ₃) ₄	5	53
DME	Br	H_2O	$Pd(Ph_3)_4$	1.5	59
DME	Br	none	$Pd(Ph_3)_4$	2	9
DME	Br	H ₂ O	$Pd(Ph_3)_4$	1.75	21
	DME DME benzene benzene NMP DME DME DME DME DME DME DME DME	DME I DME I benzene I benzene I benzene I NMP Br DME Br	DME I Na ₂ CO ₃ DME I Na ₂ CO ₃ benzene I Na ₂ CO ₃ benzene I H ₂ O benzene I Na ₂ CO ₃ NMP Br H ₂ O DME Br H ₂ O DME Br H ₂ O/TMEDA* DME Br Na ₂ CO ₃ DME Br Na ₂ CO ₃ DME Br Na ₂ CO ₃ DME Br H ₂ O DME Br none	DME I Na₂CO₃ Pd(PPh₃)₄ DME I Na₂CO₃ Pd(PPh₃)₄ benzene I Na₂CO₃ Pd(PPh₃)₄ benzene I H₂O Pd(PPh₃)₄ benzene I Na₂CO₃ Pd(PPh₃)₄ NMP Br H₂O Pd(PPh₃)₄ DME Br H₂O Pd(PPh₃)₄ DME Br H₂O/TMEDA* Pd(PPh₃)₄ DME Br Na₂CO₃ Pd(PPh₃)₄ DME Br Na₂CO₃ Pd(PPh₃)₄ DME Br Na₂CO₃ Pd(Ph₃)₄ DME Br H₂O Pd(Ph₃)₄ DME Br none Pd(Ph₃)₄	DME I Na ₂ CO ₃ Pd(PPh ₃) ₄ 20 DME I Na ₂ CO ₃ Pd(PPh ₃) ₄ 2 benzene I Na ₂ CO ₃ Pd(PPh ₃) ₄ 16 benzene I H ₂ O Pd(PPh ₃) ₄ 16 benzene I Na ₂ CO ₃ Pd(PPh ₃) ₄ 16 benzene I Na ₂ CO ₃ Pd(OAc) ₂ (PPh ₂) ₂ 20 NMP Br H ₂ O Pd(PPh ₃) ₄ 17 DME Br H ₂ O Pd(PPh ₃) ₄ 1.5 DME Br H ₂ O/TMEDA* Pd(PPh ₃) ₄ 1.5 DME Br Na ₂ CO ₃ Pd(OAc) ₂ (PPh ₃) ₂ 2 DME Br Na ₂ CO ₃ Pd(OAc) ₂ (PPh ₃) ₂ 2 DME Br Na ₂ CO ₃ Pd(PPh ₃) ₄ 1.5 DME Br Na ₂ CO ₃ Pd(PPh ₃) ₄ 2 DME Br Na ₂ CO ₃ Pd(PPh ₃) ₄ 2 DME Br Na ₂ CO ₃ Pd(Ph ₃) ₄ 5 DME Br H ₂ O Pd(Ph ₃) ₄ 1.5 DME Br DME Br Done Pd(Ph ₃) ₄ 1.5

 $^{^{}o}$ Yield obtained by distillation and NMR analysis of the distillate. b Aryllithium generated by halogen—metal change of iodobenzene in ether at -95 $^{\circ}$ C for 10 min. c 16% yield of butylbenzene. d 12% yield of butylbenzene. e 1.0 equiv of TMEDA was added. f Boronic acid prepared from phenylmagnesium chloride.

Table 2. Cross Coupling of in Situ Generated Organoboranes with Organo Halides

						_	
entry	halide	boronic acid source	catalyst	solvent	water source	time (h)	product (% yield)
1	bromobenzene	5	Pd(PPh ₃) ₄	benzene	H ₂ O	15	10 (55)
2	iodobenzene	iodobenzene	Pd(PPh ₃) ₄	benzene	2 M Na ₂ CO ₃	20	biphenyl (85)
3	bromobenzene	n-BuLi	Pd(OAc)2(PPh3)2	THF	H_2O	20	n-butylbenzene (52)
4	2-bromobenzaldehyde	benzyllithium	$Pd(PPh_3)_4$	toluene	2 M Na ₂ CO ₃	20	2-benzylbenzaldehyde (83)
5	bromobenzene	6	$Pd(PPh_3)_4$	benzene	2 M Na ₂ CO ₃	16	11 (95)
6	bromobenzene	7	$Pd(PPh_3)_4$	THF	H ₂ O	48	12 (39)
7	bromobenzene	s-BuLi	$Pd(OAc)_2(PPh_3)_2$	benzene	H_2O	16	mixture (<30)
8	3	8	$Pd(PPh_3)_4$	THF	H_2O	19	13 (43)
9	4	9	$Pd(PPh_3)_4$	DME	H_2O	2	14 (72)

Schemes:

Scheme 1

R
OR₁
Si(t-Bu)Me₂
1) B(OMe)₃,
$$0^{\circ}$$
C, 1n;
then edd 10 meHc $Pd(PPh_3)_4$,
$$1 R = R_1 = LI$$

$$2 R = Sn(Bu)_3$$
, $R_1 = H$

Scheme 1

OH
Si(t-Bu)Me₂

$$H_2O$$
, R_2 Br, 80° C, 4h
$$R_2 = Sn(Bu)_3$$
, $R_1 = H$

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