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Heck-type coupling *vs* conjugate addition in phosphine-rhodium catalyzed reactions of aryl boronic acids with α,β-unsaturated carbonyl compounds: A systematic investigation

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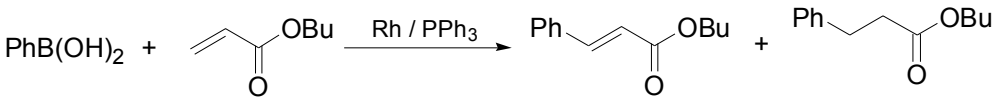
General

All reactions were performed in N_2 atmosphere unless otherwise indicated. All the commercially available chemicals were used as received. Aryl boronic acids, dppp, dppf, dppe, dppb, dppm, (±)binap and MVK were purchased from Aldrich-Sigma or Across. Vinyl phenyl ketone was prepared according to the previously reported procedure.[11] ^{1}HNMR spectra were recorded on a Bruker 500 spectrometer using the residue of deuterated solvent ($CDCl_3$) as the internal standard. GC/GC-MS analysis was performed using a Hewlett Packard Model HP 6890 Series with HP-5 column.

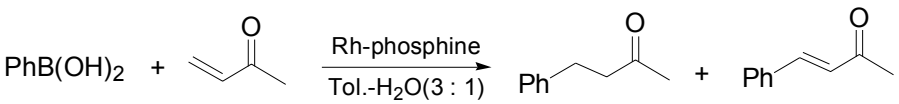
Table 1 HC/CA selectivity in the reaction of butyl acrylate with phenyl boronic acid under various conditions



Entry	B/O	Catalyst	Base[a]	T(^{o}C)	t(h)	HC/CA[b]	Yield(%)[c]
1	1/2	3%$RhCl_3$-12%PPh_3	K_2CO_3	120	5	100/0	85
2	1/2	3%$RhCl_3$-12%PPh_3	/	120	20	100/0	89
3	1/2	3%$RhCl(PPh_3)_3$	K_2CO_3	120	3	99/1	85
4	1/2	3%$RhCl(PPh_3)_3$	/	120	6	99/1	90
5[d]	1/2	3%$RhCl(PPh_3)_3$-$RhCl_3$	/	120	18	100/0	70
6[e]	1/2	3%$RhCl(PPh_3)_3$-PPh_3	/	120	5	99/1	80
7[f]	1/2	3%$RhCl(PPh_3)_3$	NH_4Cl	120	48	98/2	78
8	1/2	3%$RhCl(PPh_3)_3$	K_2CO_3	80	3	100/0	91
9	1/2	3%$RhCl(PPh_3)_3$	/	80	3	100/0	93
10[e]	1/2	3%$RhCl(PPh_3)_3$-PPh_3	/	80	5	100/0	83
11[g]	1/2	3%$RhCl(PPh_3)_3$	K_2CO_3	80	10	99/1	88
12[h]	1/2	3%$RhCl_3$-12%PPh_3	K_2CO_3	120	5	99/1	90
13	2/1	3%$RhCl_3$-12%PPh_3	/	80	20	91/9	63
14	2/1	3%$RhCl_3$-30%PPh_3	/	80	20	88/12	65
15	2/1	3%$RhCl_3$-30%PPh_3	K_2CO_3	80	8	92/8	60
16	2/1	3%$RhCl(PPh_3)_3$	/	80	8	93/7	61
17	2/1	3%$RhCl(PPh_3)_3$	/	120	8	94/6	62
18	2/1	3%$RhCl(PPh_3)_3$	K_2CO_3	80	8	89/11	71
19	4/1	3%$RhCl(PPh_3)_3$	K_2CO_3	80	8	74/26	75
20[g]	2/1	3%$RhCl(PPh_3)_3$	/	80	10	70/30	64
21[i]	2/1	3%$RhCl(PPh_3)_3$	/	80	10	90/10	62
22	1/2	3%$RhCl_3$-12%PCy_3	K_2CO_3	120	3	70/30	80
23	2/1	3%$RhCl_3$-30%PCy_3	/	80	10	55/45	54

[a] 3equiv. used. [b] Determined by ^{1}HNMR and no cis isomer of HC product detected. [c] Isolated yield (%). [d] 3%$RhCl_3$ added. [e] 15%PPh_3 added. [f] Saturated NH_4Cl(aq.) used. [g] Dioxane-H_2O(3/1, v/v) used as solvent. [h] Run in air. [i] DMF-H_2O (3/1, v/v) used as solvent.

Table 2 HC/CA selectivity in the reaction of phenyl boronic acid with MVK under various conditions



Entry	B/O	Phosphine	T(^{o}C)	T(h)	HC/CA[a]	Yield(%)[b]
1	1/2	3%$RhCl(PPh_3)_3$	120	15	73/27	89
2	1/2	3%$RhCl(PPh_3)_3$	80	15	73/27	81
3	1/3	3%$RhCl(PPh_3)_3$	80	15	85/15	96
4	1/4	3%$RhCl(PPh_3)_3$	80	15	84/16	94
5	1/8	3%$RhCl(PPh_3)_3$	80	15	87/13	93
6	1/8	3%$RhCl(PPh_3)_3$	120	15	88/12	97
7	1/1	3%$RhCl(PPh_3)_3$	80	15	46/54	58
8	2/1	3%$RhCl(PPh_3)_3$	80	15	0/100	56
9	2/1	3%$RhCl_3$-20%PPh_3	80	36	0/100	55
10	1/4	3%$RhCl_3$-6%dppf	120	24	1/99	65
11	1/4	3%$RhCl_3$-6%dppe	120	24	30/70	38
12	1/4	3%$RhCl_3$-6%dppb	120	24	1/99	75
13	1/4	3%$RhCl_3$-6%dppm	120	24	39/61	46
14	1/4	3%$RhCl_3$-6%dppp	120	24	1/99	75
15	1/4	3%$RhCl_3$-6%binap	120	24	0/100	51
16	1/1	3%$RhCl_3$-15%binap	80	36	1/99	56
17	2/1	3%$RhCl_3$-15%binap	80	36	0/100	84
18	2/1	3%$RhCl_3$-15%dppf	80	36	0/100	20
19	2/1	3%$RhCl_3$-15%dppm	80	36	0/100	21[c]
20	2/1	3%$RhCl_3$-15%dppe	80	36	0/100	17[c]
21	2/1	3%$RhCl_3$-15%dppb	80	36	0/100	31[c]
22	2/1	3%$RhCl_3$-15%dppp	80	36	0/100	11[c]

[a] Determined by ^{1}HNMR and no cis isomer of HC product detected. [b] isolated yield (%). [c]Determined by GC.