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Rhodium(I)-Catalysed Hydroboration Of 1-Halo-1-Alkenes

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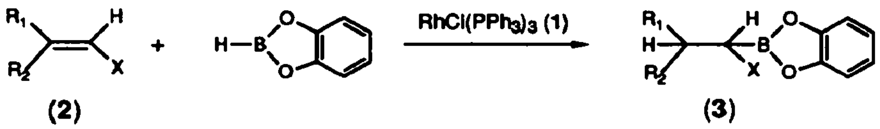
Abstract: The hydroboration of 1-halo-1-alkenes by catecholborane is accelerated by a catalytic amount of Wilkinson's catalyst {$RhCl(PPh_3)_3$} to give α-halo boronic esters in good yields.

In our previous paper[1] we have reported the synthesis of α-haloboronic esters as precursors for novel thrombin inhibitors[2,3], by refluxing catecholborane with the corresponding α-haloalkene. The reaction was monitored by the disappearance of the olefinic proton in the ^1H nmr such that no dehalogenated products were formed which could be observed in significant amounts due to extended refluxing.

The hydroboration of simple alkenes with 1,3,2-benzodioxaborole (catecholborane) in the presence of rhodium complexes has raised the possibility to extend the utility of this reaction[4,5]. In the present study, we have found that the hydroboration of an α-haloalkene (2) with catecholborane, which requires a temperature of 80-90°C without catalyst[1], occurs without difficulty at room temperature in the presence of the rhodium catalyst (1).



(2) (3)

As a general procedure, in the presence of Wilkinson's catalyst (0.05-0.5% mol. equiv.), catecholborane (45mmol, 5.4g) was added dropwise to 1-halo-1-alkene

(30 mmol) in benzene (5ml), using techniques for handling air sensitive material[6]. The reaction mixture was left stirring at room temperature, and monitored by the disappearance of the olefinic protons from the ^1H nmr spectrum, until the reaction was complete. The desired product was isolated by distillation (using a Kugelrohr distillation apparatus under vacuum) in quantitative yields as shown in the Table.

As reported previously[1], we observe that chloro alkenes (Entry 4,5) react slower than the bromo alkenes (Entry 5,9). 1,2-Dichloroalkene failed to react with catecholborane giving the starting material (entry 6).

Table Hydroboration of $R_1R_2C{=}CHX$ with catecholborane in the presence of (1)

Entry	R_1	R_2	X	Catalyst mol %	Reaction time(h)	% yield of 3[a]
1	H	H	Br	0.1	38	73
2	Me	H	Br	0.1	8	82
3	$Me(CH_2)_3$	H	Br	0.5	48	54
4	Me	Me	Cl	0.2	24	70
5	Me	Me	Br	0.05	28	98
6	Cl	H	Cl	0.5	72	-
7	Br	H	Br	0.1	24	65
8	$ClCH_2$	H	Cl	0.2	30	71
9	$BrCH_2$	H	Br	0.1	5	79
10	Ph	H	Br	0.1	30	87

a)Yield of isolated, characterised pure product.

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