Allylboranes in palladium-catalysed cross-coupling reactions†

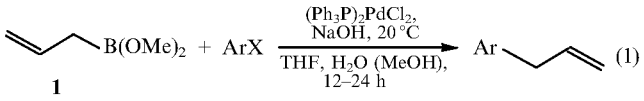
Valery N. Kalinin,* Fedor S. Denisov and Yurii N. Bubnov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: vkalin@ineos.ac.ru

A series of allylarenes have been prepared in good yields *via* palladium(II) catalysed cross-coupling reactions of allylboranes and iodoarenes in the presence of sodium hydroxide.

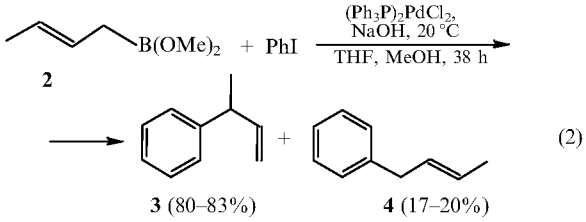
Palladium-catalysed cross-coupling reactions of Ar–X with alkyl and alkenylboranes (Suzuki–Miyaura reaction),[1,2] as well as with alkynylborates,[3] have found a wide utility in organic chemistry. Here we report the first examples of application of allylic borane coupling reactions to the synthesis of 3-arylprop-1-enes.

Allyl(dimethoxy)borane **1** reacts with aryl and heteroaryl iodides at room temperature (12–24 h) in THF in the presence of palladium catalyst and solid NaOH to produce the corresponding allylarenes in good yields (equation 1, Table 1). Yields were typically 70–95% as judged by GC. A small amount of water or alcohol should be added to the reaction mixture. Bis(triphenylphosphine)palladium(II) chloride was found to be the catalyst of choice.



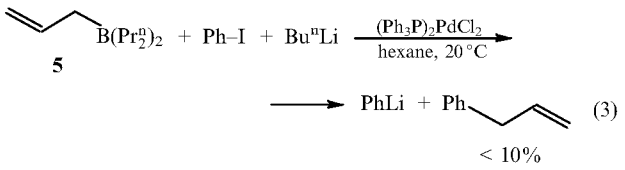
Under similar conditions, bromobenzene reacts slowly with borane **1**. The reaction ceases in 48 h, metallic palladium is precipitated, and the yield of allylbenzene does not exceed 40%.

The transposition of the allylic moiety from borane molecule to aromatic ring is accomplished predominantly by allylic rearrangement. Thus, the mixture of 3-phenylbut-1-ene **3** and *trans*-crotylbenzene **4** was isolated in 94% overall yield from the reaction of iodobenzene with crotyl(dimethoxy)borane **2** (equation 2).



A similar result was recently observed by Maeda and Miyaura in the reaction of tricrotylborane with PhI in the presence of $Pd(PPh_3)_4$ and aqueous NaOH.[4]

The interaction of allyldipropylborane **5** and iodobenzene in the presence of 1.5 mol% $(Ph_3P)_2PdCl_2$ and 0.5–1.0 equiv. of BuLi in hexane is accompained by the exchange of iodine by lithium and the yield of allylbenzene does not exceed 5–10%.



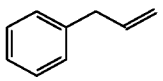
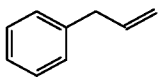
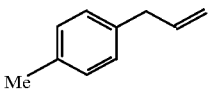
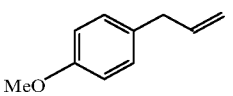
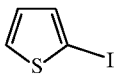
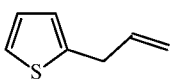
Allylbenzene was not found in the reaction of PhI with **1** or **5** under Pd^0 or Pd^{II} catalysts in experiments not using sodium hydroxide. The latter result shows clearly that the presence of NaOH is of considerable significance in cross-coupling reactions with allylboranes.

To a stirred solution of iodobenzene (1.02 g, 5 mmol), $(Ph_3P)_2PdCl_2$ (0.07 g, 0.1 mmol), dodecane (0.42 g) as the internal standard and **1** (0.78 g, 5.6 mmol) in 8 ml THF, were successively added NaOH (0.8 g, 20 mmol) and MeOH (0.5 ml). The mixture was then stirred at room temperature for 12–24 h. The yields were determined by GLC (Table 1).

To a stirred solution of iodobenzene (5.1 g, 25 mmol), $(Ph_3P)_2PdCl_2$ (0.2 g, 0.2 mmol) and **2** (4.5 g, 35.1 mmol) in 50 ml THF were added solid NaOH (5.6 g, 140 mmol) and then 3 ml MeOH (dropwise). The mixture was stirred for 38 h at room temperature. (According to GLC the reaction mixture contained a small quantity of butenes, solvents and two products; the starting PhI was absent). Water (10 ml) was added and products were extracted with hexane (3 × 20 ml), dried over Na_2SO_4 and solvents were removed *in vacuo*. The yield was 3.1 g (94%), bp 95–96 °C/18 mmHg. According to GLC and NMR spectra, the products were a mixture of **3** and **4** in the ratio 4 : 1. The ^1H and ^{13}C NMR spectra are in accordance with those described in ref. 5.

Thus, we have developed an effective route for the transfer of allylic substituents in boronic ethers to organic groups under very mild conditions. Studies in this direction are currently in progress.

Table 1 Cross-coupling of aryl halides with $CH_2=CHCH_2B(OMe)_2$ in the presence of $(Ph_3P)_2PdCl_2$ at 20 °C.

Entry	Ar–X	*t*/h	Product	Yield (%)
1	PhI	24		98
2	PhBr	48		40
3	*p*-MeC_6H_4I	18		91
4	*p*-$MeOC_6H_4I$	12		80
5		20		70
6	PhI[a]	38	**3** + **4** (ratio 4 : 1)	94

[a] Crotyl(dimethoxy)borane was used as an allylating reagent.

† Partially presented at The VI[th] All-Russian Conference on Organometallic Chemistry, Nizhnii Novgorod, 1995, p. 361 (in Russian).

The authors are grateful to the Russian Foundation for Basic Research for financial support (project no. 96-03-33376).

References

1 A. Suzuki, *Pure Appl. Chem.*, 1991, **63**, 419 and references therein.
2 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
3 J. A. Soderquist, K. Matos, A. Rane and J. Ramos, *Tetrahedron Lett.*, 1995, **30**, 2401.
4 K. Maeda and N. Miyaura, unpublished data; see ref. 3, p. 2476.
5 R. Bussas, H. Munstere and G. Kresze, *J. Org. Chem.*, 1983, **48**, 2828.

Received: Moscow, 16th May 1996
Cambridge, 10th June 1996; Com. 6/03521C