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THE SYNTHESIS OF BIALKYLS AND BIARYLS FROM GRIGNARD REAGENTS VIA ORGANOBORANES

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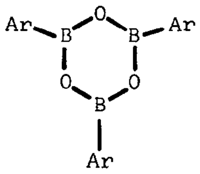
The reaction of alkyl boronic acids with ammoniacal silver oxide was reported by Johnson and his collaborators[1,2] to give good yields of bialkyls. Under the same conditions aryl boronic acids underwent deboronation to give the corresponding arenes[2,3]; no biaryls could be formed this way. Brown has subsequently found that treatment of organoboranes, obtained from the reaction of olefins with diborane, with alkaline silver nitrate offered a convenient general method for the synthesis of symmetrical[4] and unsymmetrical[5] bialkyls. We have recently developed a convenient new route to organoboranes[6] by reacting alkyl or aryl halides with magnesium in the presence of diborane. We now report that treatment of both alkyl and arylboranes prepared in this way, with alkaline silver nitrate gives good yields of bialkyls and biaryls.

The procedure is experimentally very simple. The organoborane is formed by reacting the halide (20 millimole) with magnesium (20 milliatom) in the presence of BH_3 (30 millimole) in refluxing tetrahydrofuran solution[6]. The organoborane thus formed is then reacted with potassium hydroxide in methanol and aqueous silver nitrate[4] to accomplish the coupling. Typical results are shown in the Table.

The reaction appears to be successful for aryl, secondary and primary alkyl halides and thus it has somewhat wider applicability than the comparable method for coupling Grignard reagents using TlBr[7]. In agreement with McKillop's observations[7] we find the coupling reaction to be quite sensitive to steric hindrance. When 2-bromotoluene was used in the reaction, the yield of 2,2' dimethylbiphenyl was only 17% and this was accompanied by a 45% yield of tri-o-tolyl boroxine. Using mesityl bromide, the only product isolated was trimesitylboroxine in 86% yield[8].



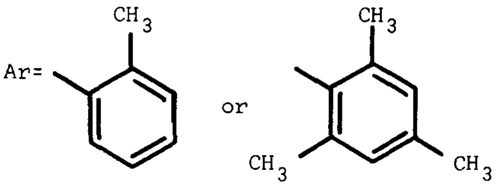


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Table

Halide	Product	Yield (%)
bromobenzene	biphenyl	59
3-bromoanisole	3,3' dimethoxybiphenyl	52
4-dimethylaminobromobenzene	N,N,N',N' tetramethylbenzidine	71
4-bromotoluene	4,4' dimethylbiphenyl	70
3-iodochlorobenzene	3,3' dichlorobiphenyl	60
bromocyclohexane	bicyclohexyl	71
1-bromo octane	n-hexadecane	90
1-bromohexane	n-dodecane	94
benzylbromide	1,2-diphenylethane	85
1-bromo-2-phenoxyethane	1,4-diphenoxy-n-butane	83

The yields of biaryls refer to isolated purified products; m.p.'s were in agreement with published data. The yields of bialkyls were estimated by G.L.C.

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8. The boroxine structure for the anhydride of mesityl boronic acid has been questioned (R.T. Hawkins, W.J. Lennarz and H.R. Snyder, J.Amer.Chem.Soc., 82, 3053 (1960)). Our compound had a mass spectrum compatible with the trimer structure $(ArBO)_3$. Details of the mass spectrum and other properties of trimesitylboroxine will be published in the near future.