

## Nickel-induced Conversion of Carbon–Nitrogen into Carbon–Carbon Bonds. One-step Transformations of Aryl, Quaternary Ammonium Salts into Alkylarenes and Biaryls

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Aryltrimethylammonium iodides are shown to undergo reaction with Grignard reagents under phosphine-ligated, low-valent nickel catalysis with the formation of alkylarenes and biaryls.

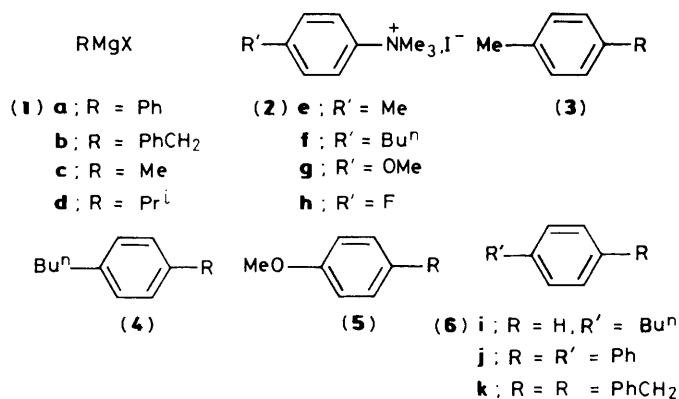
Some time ago there was introduced a new method of carbon–carbon bond formation based on the replacement of the alkoxy group of vinyl or aryl ethers by an alkyl or aryl substituent on exposure of the ethers to Grignard reagents under phosphine-ligated, low-valent nickel catalysis.<sup>1</sup> This discovery was followed by a second procedure involving the replacement of the alkylthio unit of vinyl or aryl thioethers by alkyl or aryl functions under similar circumstances.<sup>2</sup> The

logical goal, *i.e.* the replacement of the dialkylamino moiety of enamines or arylamines, remained elusive.† Here we show that the goal now has been achieved *via* the nickel-catalysed Grignard reactions of quaternary anilinium salts (Scheme 1).



Scheme 1. i: [PPh<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>]NiCl<sub>2</sub>, Et<sub>3</sub>N, benzene, heat.

The reactions were carried out with Grignard reagents (**1a–d**) on salts (**2e–h**) in refluxing benzene solution in the presence of triethylamine and [1,3-bis(diphenylphosphino)propane]-nickel dichloride. The results are listed in Table 1. Every reaction was accompanied by some *N*-demethylation, yielding *N,N*-dimethylanilines. The latter were the sole products of



† On the assumption of the nitrogenous sidechain requiring leaving group characteristics for the success of the Grignard reaction, the following aniline derivatives have been tested: *p*-toluenesulphonyl-*N*-methyl-*p*-*n*-butylanilide, bis-*p*-toluenesulphonyl-*p*-*n*-butylanilide, bis-trifluoromethanesulphonyl-*p*-*n*-butylanilide and *p*-*n*-butylphenylisocyanide. However their nickel-catalysed interaction with methylmagnesium or phenylmagnesium bromide led to neither *p*-*n*-butyltoluene nor *p*-*n*-butylbiphenyl, respectively (E. Wenkert, J. M. Hanna, Jr., and C.-J. Jenny, unpublished observations).

**Table 1.** Reactions of Grignard reagents (1) with anilinium iodides (2).<sup>a</sup>

Entry	Grignard reagent <sup>b</sup>	Salt	Product	Yield (%)
1	(1a)	(2e)	(3a)	31 <sup>k</sup>
2	(1b)	(2e)	(3b) <sup>c</sup>	63 <sup>k</sup>
3	(1b)	(2f)	(4b) <sup>d</sup>	60 <sup>k</sup>
4	(1c)	(2f)	(4c) <sup>e</sup>	26
5	(1d)	(2f)	{(4d) <sup>f</sup> {(6i)	{20 {11
6	(1a)	(2g)	{(5a) <sup>g</sup> {(6j)	{23 {13
7	(1b)	(2g)	(5b) <sup>h</sup>	47
8	(1c)	(2g)	(5c)	20
9	(1d)	(2g)	(5d) <sup>i</sup>	18
10	(1b)	(2h)	(6k) <sup>j</sup>	37

<sup>a</sup> A benzene solution (20 ml) of Grignard reagent (3 mmol), anilinium salt (1 mmol), triethylamine (15 mmol), and [1,3-bis(diphenylphosphino)propane]nickel dichloride (0.1 mmol) was refluxed for 14 h. Yields are based on products isolated. <sup>b</sup> X = Br for (1a), (1c), and (1d); X = Cl for (1b). <sup>c</sup> Ref. 4. <sup>d</sup> Ref. 5. <sup>e</sup> Ref. 6. <sup>f</sup> Ref. 7. <sup>g</sup> Ref. 8. <sup>h</sup> Ref. 9. <sup>i</sup> Ref. 10. <sup>j</sup> Ref. 11. <sup>k</sup> By <sup>1</sup>H n.m.r. spectral analysis.

reactions carried out without nickel catalyst (tested on the reaction of Table 1 entries 1–3, 6, and 8). Isopropylmagnesium bromide acted not only as an isopropylation agent

(entries 5 and 9), but also to some extent as a reducing system (entry 5).<sup>3</sup> Finally, the trimethylamine extrusion was accompanied by the replacement of methoxy (entry 6)<sup>1</sup> and fluoro groups (entry 10).

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