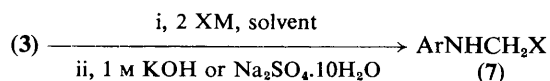


Scheme 2. Reagents: i, MeLi, Et₂O, -60 °C; ii, BuⁿLi, Et₂O, -60 °C, then 1 M KOH.



Scheme 3

methyl-lithium and then with *n*-butyl-lithium, *N*-pentylaniline (7b) was obtained uncontaminated with *N*-ethylaniline (Scheme 2). This result can be easily rationalized through the formation of the stable (-60 °C) monomeric methyleneamine (1a) via β-elimination of lithium methoxide from the lithium amide (6), and represents the first case in which a methyleneamine is trapped and then allowed to react in a directed way. When *s*-triazines were treated under similar conditions as (3a) in Scheme 2, they were recovered unchanged.

Based on this behaviour a new and simple method for the selective monoalkylation of primary arylamines has been developed. *N*-(Methoxymethyl)arylamines are allowed to react with the organometallic (Li or Mg) reagent XM in ether or pentane solution at -60 or 0 °C leading to the corresponding alkylarylamines (7), isolated in good yields (Scheme 3, Table 2).

Our method of alkylation affords the alkylamines (7) in which the nitrogen is bonded to a primary carbon atom, and has the advantage that the product is uncontaminated with either the corresponding arylamine or the bisalkylated compound. It is noteworthy that most of the existing methods for

Table 2. Synthesis of the *N*-alkylarylamines ArNHCH₂X (7) from (3) and the organometallic reagents XM.^a

(3)	XM	(7)			
		Ar	X		
(3a)	MeLi	a	Ph	Me	93 ^d
(3a)	Bu ⁿ Li	b	Ph	Bu ⁿ	87
(3a)	PhLi	c	Ph	Ph	92 ^e
(3a)	Pr ⁿ MgBr ^b	d	Ph	Pr ⁿ	74
(3a)	c-C ₅ H ₉ Li ^c	e	Ph	c-C ₅ H ₉	95
(3e)	Bu ⁿ Li	f	<i>m</i> -MeC ₆ H ₄	Bu ⁿ	94
(3e)	Bu ^t Li ^b	g	<i>m</i> -MeC ₆ H ₄	Bu ^t	88

^a Reactions were carried out in ether at 0 °C unless otherwise noted. Known compounds were identified by comparison with authentic samples. New compounds showed i.r. and n.m.r. spectra and elemental analyses consistent with the assigned structures. ^b At -60 °C. ^c In pentane; c-C₅H₉ = cyclopentyl. ^d Ref. 7(a). ^e Ref. 7(b).

the alkylation of amines suffer from lack of selectivity for monoalkylation, particularly when primary or benzyl groups are to be introduced, unless alkylations are performed with a large excess of primary amine which finally becomes the main component in the product reaction mixture.

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