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SYNTHESIS OF ARYLIMINES FROM N-SILYLAMIDES AND ARYLLITHIUM COMPOUNDS

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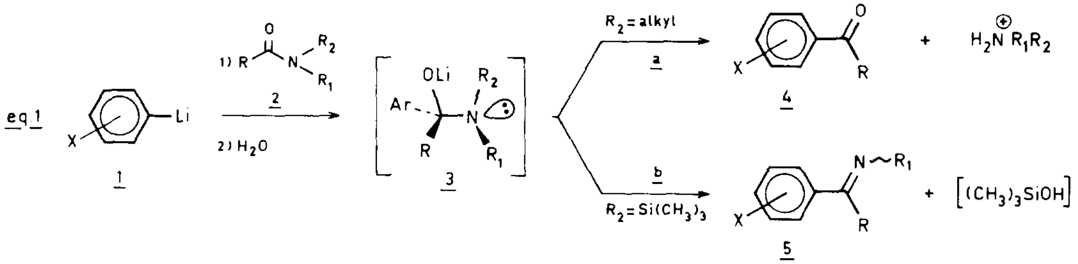
Abstract: Various arylimines were synthesized by the addition of N-silylated-N-alkyl-or N-aryl-amides to aryllithium compounds.

The addition reaction of organolithium compounds 1 to the carbonyl group of N,N-disubstituted amides 2 is well known to yield carbonylcompounds 4 (eq. 1a).[1,2] This reaction is particulary valuable in the synthesis of aldehydes from DMF[1,2] or N-methylformanilide[3] whereas N-(2-pyridyl)-N-methylformamide[4] is preferred for similar reactions with Grignard reagents.



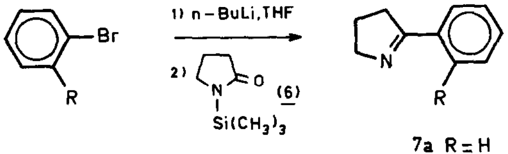
(X = H, CH_3, OCH_3; R = H, alkyl, aryl; R_1 = alkyl, aryl)

In connection with synthetic studies using N-silylated-amides[5] 2 (R_2=Si$(CH_3)_3$ and N-silylated-lactams[5] we have found that aryllithium compounds 1 readily react with amides 2 to give imines[6] 5 instead of carbonyl compounds 4 (eq. 1b).

Treatment of a solution of phenyllithium in THF at -78°C with N-methyl-N-trimethylsilyl propionamide, either neat or as a solution in THF, and subsequent warming to room temperature gave after a standard work-up, N-methyl-ethylphenylimine in 73% yield. The results of the conversion of aryllithium compounds with several N-silylated amides are summarized in Table I. The imineformation is strongly dependant on the basicity of the lithium reagent as alkyllithium compounds only yielded products derived from deprotonation of the N-silylated acetamides. Isomerically pure imines were obtained from all formamides (entries 6, 10, 11) and N-methyl-N-trimethylsilylacetamides (entries 3, 7). The stereochemical assignment is based on comparison of ^{1}H-NMR data with those published. For the acetophenone- and 2-acetylfuran-imines (entries 3, 7), the E-configuration was established on basis of the observed coupling constants in the ^{1}H-NMR spectra ($J_{H,H}$ < 1.0 Hz for HC-C=N-CH).[7]

The imines 5 can be reduced in situ to amines [71%, ($NaBH_4$, CH_3OH); 75%, 83% and 60%, ($LiAlH_4$, THF) for entries 1, 2, 3 and 4 respectively] or hydrolysed to aldehydes or ketones (e.g. entry 1, 80% phenylethylketone).

eq. 2

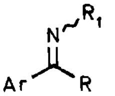


7a R = H (20%)

7b R = OCH_3 (43%)

The present method also allows preparation of aryl-Δ^1-pyrrolines 7 from N-silylated-pyrrolidone 6, although yields are low sofar. Thus reaction of phenyllithium with 6 gave 20% of 7 after chromatography (identical with an independently prepared sample[8]) (eq. 2).

Table I Synthesis of Arylimines



	Aryl-	R	R_1	yield(%)[a]	Z/E[b]
1	C_6H_5	C_2H_5	CH_3	73	30/70
2	C_6H_5	CH_3	C_2H_5	60	40/60
3	C_6H_5	CH_3	CH_3	63	0/100
4	C_6H_5	C_6H_5	CH_3	77	-
5	C_6H_5	C_6H_5	C_6H_5	80	-
6	C_6H_5	H	C_6H_5	55	0/100
7	C_4H_3O	CH_3	CH_3	57	0/100
8	C_4H_3O	C_6H_5	CH_3	55	40/60
9	C_4H_3O	C_6H_5	C_6H_5	79	45/55
10	C_6H_5	H	CH_3	35	0/100
11	(o-OCH_3)C_6H_5	H	C_6H_5	70	0/100

a. Isolated yield by distillation; b. Z/E ratio determined by NMR.

The elucidation of the stereochemical features of this new imine formation and the use of functionalized organolithium reagents is presently under investigation.

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