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Organolithium Reagents by Reductive Decyanation of Nitriles with Lithium and a Catalytic Amount of 4,4'-Di-*tert*-butyl-biphenyl in a Barbier-Type Reaction

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Abstract: The reaction of different nitriles **1** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (5 mol %) in the presence of a carbonyl compound (Barbier-type conditions) in THF at low temperature (-30 or -78°C) leads to the corresponding compounds **2** resulting from the coupling between the electrophile and the organolithium intermediate arising from a reductive decyanation of the starting nitrile **1**. This new reaction can be also applied to the use of trimethylchlorosilane as electrophile at 0°C.

INTRODUCTION

Although in some cases (tertiary derivatives) the reduction of nitriles to primary amines with dissolving metals leads to significant decyanation[1], in general, the corresponding amines can be obtained in reasonable to excellent yields[2]. Generally, lithium, sodium or calcium in liquid ammonia or methylamine are adequate reagents for this transformation[2,3]. On the other hand, we have recently discovered that a mixture of lithium powder and a catalytic amount of an arene in THF is a very powerful lithiating agent[4], which can be used for the preparation of very unstable functionalised organolithium reagents[5] by chlorine-lithium[6] exchange at low temperature or for the lithiation of other systems such as sulfonates[7a] or sulfates[7b], oxygen- or nitrogen-containing heterocycles[8], or carbonyl derivatives[9] under very mild reaction conditions. In this paper we use this arene-catalysed lithiation[10] process[4] with 4,4'-di-*tert*-butylbiphenyl for the reductive decyanation of nitriles yielding organolithium reagents, which in the presence of a carbonyl compound or trimethylchlorosilane (Barbier-type conditions) yield the expected coupling products.

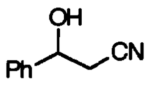
RESULTS AND DISCUSSION

The reaction of different nitriles **1** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (1:0.1 molar ratio; 5 mol %) in THF at low temperature (see Table 1) in the presence of a carbonyl compound (Barbier-type reaction conditions) led, after hydrolysis with aqueous hydrochloric acid, to the corresponding products **2** resulting from the substitution of the cyano group by an electrophile (Scheme 1 and Table 1). In general, this decyanation process, which leads to an organolithium intermediate RLi, was carried out at -30°C (Table 1, entries 1-10), except in the case of starting from benzyl cyanide, in which it is necessary to perform the reaction at -78°C in order to avoid undesirable by-reaction (Table 1, entries 12-14); under these last reaction conditions some of the starting material **1d** was recovered (8-17%) unchanged at the end of the process, the decyanation step being an incomplete reaction (Table 1, footnotes i and j). Just to test if the above described Barbier-type process can be applied to other electrophilic reagents we tried the same reaction with **1** in the presence of trimethylchlorosilane at 0°C, obtaining the expected product **2cf** in 63% isolated yield (Table 1, entry 11). When the reaction was carried out in absence of the electrophile, which was added once the lithiation finished, yields were lower; for instance, the lithiation of benzonitrile (**1e**) under the above described standard conditions (30 min) followed by reaction with cyclohexanone led to compound **2ce** in only 39% yield (Table 1, entry 10 and footnote g).

$$\underset{\mathbf{1}}{\mathrm{RCN}} \xrightarrow{\text{i,ii}} \underset{\mathbf{2}}{\mathrm{RE}}$$

Scheme 1. *Reagents and conditions*: i, Li powder (excess), 4,4'-di-*tert*-butylbiphenyl (5 mol%), E^+=Pr^iCHO, *n*-$C_7H_{15}CHO$, Me_2CO, Et_2CO, $(CH_2)_5CO$, Ph_2CO, Me_3SiCl, low temperature (see Table 1); ii, H_2O-HCl.

In general, yields are moderate due, in our opinion, to the probable consumption of the organolithium intermediate RLi deprotonating the α position of the starting nitrile, when this is possible. This by-reaction could be verified by isolation of product **3** in low yield (4%) in the reaction of acetonitrile **1a** with benzaldehyde (Table 1, entry 1). On the other hand, in all reactions a 10-15% yield of the corresponding pinacol-type products were detected by GLC; the separation of these by-products from the desired products **2** was easy by flash chromatography. When benzophenone was used as electrophile and acetonitrile as source of methyllithium, product **4** was isolated in 23% yield: the formation of this by-product can be explained by (a) addition of cyanide (resulting from the decyanation of the starting material **1a**) to the electrophile followed by addition of methyllithium to the formed cyanhydrine salt and final hydrolysis or/and (b) addition of the dianion of benzophenone[9a] to the starting acetonitrile **1a** followed by hydrolysis, this last possibility being, in our opinion, the most probable (Table 1, entry 2).



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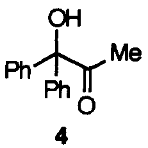

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Table 1. Reductive Decyanation of Nitriles **1** under Barbier-Type Reaction Conditions. Isolation of Products **2**

	Starting nitrile		Electrophile	Reaction	Product[a]			
Entry	No.	R	E^+	T (°C)	No.	E	Yield (%)[b]	R_f[c]
1	**1a**	Me	PhCHO	-30	**2aa**	PhCHOH	39[d]	0.34[e]
2	**1a**	Me	Ph_2CO	-30	**2ab**	Ph_2COH	32[f]	0.34
3	**1b**	c-C_3H_5	n-$C_7H_{15}CHO$	-30	**2ba**	n-$C_7H_{15}CHOH$	21	0.26
4	**1b**	c-C_3H_5	Et_2CO	-30	**2bb**	Et_2COH	47	0.47
5	**1b**	c-C_3H_5	$\overline{(CH_2)_5C}O$	-30	**2bc**	$\overline{(CH_2)_5C}OH$	25	0.31
6	**1c**	Ph	i-PrCHO	-30	**2ca**	i-PrCHOH	62	0.76
7	**1c**	Ph	PhCHO	-30	**2cb**	PhCHOH	40	0.23
8	**1c**	Ph	Me_2CO	-30	**2cc**	Me_2COH	46	0.26
9	**1c**	Ph	Et_2CO	-30	**2cd**	Et_2COH	55	0.38
10	**1c**	Ph	$\overline{(CH_2)_5C}O$	-30	**2ce**	$\overline{(CH_2)_5C}OH$	62[g]	0.28
11	**1c**	Ph	Me_3SiCl	0	**2cf**	Me_3Si	63	0.55[h]
12	**1d**	$PhCH_2$	i-PrCHO	-78	**2da**	i-PrCHOH	46(50)[i]	0.54
13	**1d**	$PhCH_2$	Et_2CO	-78	**2db**	Et_2COH	41(49)[j]	0.44
14	**1d**	$PhCH_2$	$\overline{(CH_2)_5C}O$	-78	**2dc**	$\overline{(CH_2)_5C}OH$	48(58)[j]	0.40

[a] All products **2** isolated were >95% pure (GLC and 300 MHz ^1H NMR) and were fully characterised by spectroscopic methods (IR, ^1H and ^{13}C NMR, and mass spectra). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting nitrile **1**; in parenthesis isolated yield based on the consumed starting material **1d**. [c] Silica gel, hexane/ethyl acetate: 6/1. [d] 3-Hydroxy-3-phenylpropionitrile **3** was also obtained (4%). [e] Silica gel, hexane/ethyl acetate: 4/1. [f] 1-Hydroxy-1,1-diphenylacetone **4** was also isolated (23%). [g] 39% yield in the non-Barbier procedure (see text). [h] Silica gel, hexane. [i] Benzyl cyanide **1d** was also obtained (8%). [j] Benzyl cyanide **1d** was also obtained (17%).

From the results described in this paper we conclude that this methodology permits the direct transformation of nitriles into organolithium compounds, by an arene-catalysed reductive decyanation reaction, which can be trapped with a carbonyl compound (or trimethylchlorosilane) to give the expected coupling products. This is, to our best knowledge, a new reaction, which complements the well-known reduction of nitriles to primary amines by dissolving metals[2].

EXPERIMENTAL PART

General.-For general information see reference 9b. All starting materials and the electrophiles were commercially available (Aldrich, Fluka).

Reductive Decyanation of Nitriles **1** *and Reaction with Electrophiles. Isolation of Compounds* **2**. *General Procedure.*-To a blue suspension of lithium powder (100 mg, 14 mmol) and 4,4'-di-*tert*-butylbiphenyl (26 mg, 0.10 mmol) in THF (5 ml) was slowly added (*ca.* 45 min) a solution of the starting nitrile (1 mmol) and the carbonyl compound (1.2 mmol) in THF (2 ml) at -30 or -78°C (see Table 1)[11]. After 10 min stirring at the same temperature[12] the resulting mixture was hydrolysed with water and neutralised with 2 N hydrochloric acid [CAUTION!: due to possible evolution of hydrogen cyanide the work-up should be carried out in a good ventilated hood] and extracted with diethyl ether (2x20 ml). The organic layer was dried with anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was then purified by flash chromatography (silica gel, hexane/ethyl acetate) to yield the corresponding pure products **2**. Yields and R_f values are included in Table 1. Retention times (for conditions see reference 9b) and spectroscopic data, as well as literature references for known compounds follow.

1-Phenylethanol (**2aa**)[13]: t_r 6.44 min; ν_{max} (film) 3350 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 1.46 (3 H, d, J=6.5, Me), 2.28 (1 H, br s, OH), 4.84 (1 H, q, J=6.5, CHO) and 7.23-7.38 (5 H, m, ArH); δ_C 25.05 (Me), 70.25 (CO), 125.3, 127.35, 128.4 and 145.75 (ArC); *m/z* 122 (M^+, 53%), 107 (100), 105 (11), 79 (90), 78 (18), 77 (57), 51 (17) and 43 (14).

1,1-Diphenylethanol (**2ab**)[14]: t_r 12.27 min; ν_{max} (film) 3400 (OH), 3050, 3020, 1595 and 1490 cm^{-1} (HC=C); δ_H 1.90 (3 H, s, Me), 2.29 (1 H, br s, OH) and 7.16-7.39 (10 H, m, ArH); δ_C 30.7 (Me), 76.1 (CO), 125.8, 126.85, 128.05 and 147.9 (ArC); *m/z* 199 (M^++1, 2%), 198 (M^+, 9), 184 (22), 183 (100), 121 (16), 105 (77), 78 (14), 77 (49), 51 (16) and 43 (31).

1-Cyclopropyl-1-octanol (**2ba**): t_r 9.79 min; ν_{max} (film) 3390 cm^{-1} (OH); δ_H 0.15-0.26, 0.44-0.51 (2 H each, 2 m, 2xCH_2 ring), 0.81-0.91 (1 H, m, CH ring), 0.85 (3 H, t, J=6.9, Me), 1.10-1.45, 1.53-1.61 [10 H and 2 H, respectively, 2 m, $(CH_2)_6$Me], 1.62 (1 H, br s, OH) and 2.83 (1 H, dt, J=8.3, 6.2, CHOH); δ_C 2.4, 2.75 (2xCH_2 ring), 14.05 (Me), 18.0 (CH ring), 22.65, 25.7, 29.3, 29.7, 31.85, 37.25 [$(CH_2)_6$Me] and 76.95 (CO); *m/z* 142 (M^+-28, <1%), 71 (100), 43 (30) and 41 (17).

3-Cyclopropyl-3-pentanol (**2bb**)[15]: t_r 5.30 min; ν_{max} (film) 3450 cm^{-1} (OH); δ_H 0.26 (4 H, d, J=7.0, 2xCH_2 ring), 0.70 (1 H, s, OH), 0.77 (1 H, quintet, J=7.0, CH), 0.85 (6 H, t, J=7.5, 2xMe) and 1.44 (4 H, q, J=7.5, 2xCH_2Me); δ_C -0.25 (2 C, 2xCH_2 ring), 7.95 (2 C, 2xMe), 18.6 (CH), 32.1 (2 C, 2xCH_2Me) and 72.35 (CO); *m/z* 100 (M^+-28, 4%), 99 (40), 57 (100), 43 (15) and 41 (13).

1-Cyclopropylcyclohexanol (**2bc**)[16]: t_r 7.56 min.; ν_{max} (film) 3400 cm^{-1} (OH); δ_H 0.28-0.32 (4 H, m, 2xCH_2CH), 0.84-0.91 (1 H, m, CH), 0.89 (1 H, s, OH), 1.32-1.40 and 1.47-1.58 (2 H and 8 H, respectively, 2 m, 5xCH_2 cyclohexanol); δ_C -0.15 (2 C, 2xCH_2CH), 21.75 (CH), 21.95 (2 C), 25.9, 37.25 (2 C)(5xCH_2 cyclohexanol) and 69.5 (CO); *m/z* 99 (M^+-41, 100%), 98 (45), 81 (54), 55 (16) and 41 (11).

2-Methyl-1-phenyl-1-propanol (**2ca**)[17]: t_r 8.25 min; ν_{max} (film) 3370 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.79 (3 H, d, J=6.8, 1xMe), 0.99 (3 H, d, J=6.7, 1xMe), 1.85 (1 H, s, OH), 1.95 (1 H, octet, J=6.8, CHMe), 4.35 (1 H, d, J=6.9, CHO) and 7.24-7.36 (5 H, m, ArH); δ_C 18.2, 18.95 (2xMe), 35.25 (CHMe), 80.0 (CO), 126.55, 127.4, 128.15 and 143.6 (ArC); *m/z* 151 (M^++1, 1%), 150 (M^+, 5), 107 (100), 79 (63), 77 (43) and 51 (14).

Diphenylmethanol (**2cb**)[18]: t_r 12.18 min; ν_{max} (film) 3270 (OH), 3050, 3020, 1590 and 1490 cm^{-1} (HC=C); δ_H 2.38 (1 H, br s, OH), 5.81 (1 H, s, CHO) and 7.22-7.38 (10 H, m, ArH); δ_C 76.2 (CO), 126.5, 127.5, 128.45 and 143.8 (ArC); *m/z* 186 (M^++2, 1%), 185 (M^++1, 8), 184 (M^+, 63), 183 (20), 165 (14), 107 (16), 106 (11), 105 (100), 79 (39), 78 (37), 77 (75), 51 (28) and 50 (11).

2-Phenyl-2-propanol (2cc)[19]: t_r 7.01 min; ν_{max} (film) 3380 (OH), 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 1.49 (6 H, s, 2xMe), 1.90 (1 H, br s, OH), 7.16 (1 H, t, *J*=7,5, *p*-ArH), 7.25 (2 H, dd, *J*=7.8, 7.5, *m*-ArH) and 7.40 (2 H, d, *J*=7.8, *o*-ArH); δ_C 31.65 (2 C, 2xMe), 72.45 (CO), 124.3, 126.6, 128.15 and 149.05 (ArC); *m/z* 137 (M$^+$+1, 1%), 136 (M$^+$, 12), 121 (100), 77 (14) and 43 (62).

3-Phenyl-3-pentanol (2cd)[20]: t_r 9.06 min; ν_{max} (film) 3450 (OH), 3050, 3020, 1600 and 1485 cm^{-1} (HC=C); δ_H 0.67 (6 H, t, *J*=7,5, 2xMe), 1.68-1.82 (5 H, m, 2xCH$_2$ and OH), 7.09-7.16 and 7.21-7.31 (1 H and 4 H, respectively, 2 m, ArH); δ_C 7.75 (2 C, 2xMe), 34.9 (2 C, 2xCH$_2$), 77.3 (CO), 125.4, 126.15, 127.9 and 145.7 (ArC); *m/z* 164 (M$^+$, <1%), 135 (100), 105 (11), 77 (23) and 57 (74).

1-Phenylcyclohexanol (2ce)[21]: t_r 11.08 min; ν_{max} (film) 3390 (OH), 3050, 3020, 1595 and 1490 cm^{-1} (HC=C); δ_H 1.59-1.85 (10 H, m, 5xCH$_2$ ring), 7.23-7.25, 7.31-7.36 and 7.49-7.52 (5 H, 3 m, ArH); δ_C 22.15 (2 C), 25.5, 38.8 (2 C)(5xCH$_2$ ring), 73.1 (CO), 124.55, 126.65, 128.15 and 149.4 (ArC); *m/z* 177 (M$^+$+1, 3%), 176 (M$^+$, 30), 133 (100), 120 (30), 105 (34), 91 (18), 78 (23), 77 (44), 55 (41) and 51 (15).

Trimethylphenylsilane (2cf)[22]: t_r 6.02 min; ν_{max} (film) 3050, 3010, 1595 and 1490 cm^{-1} (HC=C); δ_H 0.28 (9 H, s, 3xMe), 7.35-7.38 and 7.52-7.55 (3 H and 2 H, respectively, 2 m, ArH); δ_C -1.15 (3 C, 3xMe), 127.7, 128.75, 133.3 and 140.35 (ArC); *m/z* 152 (M$^+$+2, 1%), 151 (M$^+$+1, 2), 150 (M$^+$, 13), 136 (11) and 135 (100).

3-Methyl-1-phenyl-2-butanol (2da)[23]: t_r 9.38 min; ν_{max} (film) 3400 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.99 (6 H, d, *J*=6.8, 2xMe), 1.60 (1 H, br s, OH), 1.71-1.77 (1 H, m, C*H*Me), 2.59, 2.84 (1 H each, dd=13.6, 9.4, dd=13.6, 3.4, respectively, CH$_2$), 3.55-3.61 (1 H, m, CHO) and 7.21-7.33 (5 H, m, ArH); δ_C 17.35, 18.85 (2xMe), 33.05 (*C*HMe), 40.7 (CH$_2$), 77.45 (CO), 126.3, 128.5, 129.3 and 139.15 (ArC); *m/z* 164 (M$^+$, 2%), 121 (9), 92 (100), 91 (95), 77 (19), 65 (33) and 41 (27).

3-Benzyl-3-pentanol (2db)[24]: t_r 10.18 min; ν_{max} (film) 3430 (OH), 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.92 (6 H, t, *J*=7.5, 2xMe), 1.35 (1 H, br s, OH), 1.46 (4 H, q, *J*=7.5, 2xC*H*$_2$Me), 2.74 (2 H, s, C*H*$_2$Ph) and 7.21-7.32 (5 H, m, ArH); δ_C 7.95 (2 C, 2xMe), 30.4 (2 C, 2x*C*H$_2$Me), 44.75 (*C*H$_2$Ph), 74.55 (CO), 126.3, 128.15, 130.55 and 137.95 (ArC); *m/z* 178 (M$^+$, 3%), 149 (30), 92 (100), 91 (92), 87 (93), 65 (30) and 57 (38).

1-Bencylcyclohexanol (2dc)[25]: t_r 11.89 min; ν_{max} (film) 3380 (OH), 3080, 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 1.34 (1 H, br s, OH), 1.38-1.56 (10 H, m, 5xCH$_2$ ring), 2.72 (2 H, s, C*H*$_2$Ph) and 7.18-7.30 (5 H, m, ArH); δ_C 22.05 (2C), 25.7, 37.2 (2C)(5xCH$_2$ ring), 48.65 (*C*H$_2$Ph), 71.05 (CO), 126.25, 128.0, 130.55 and 137.15 (ArC); *m/z* 190 (M$^+$, 1%), 99 (93), 92 (100), 91 (79), 81 (61), 65 (24) and 55 (18).

3-Hydroxy-3-phenylpropionitrile (3)[26]: t_r 10.51 min; ν_{max} (film) 3410 (OH), 3050, 3020, 1600, 1490 (HC=C) and 2250 cm^{-1} (C≡N); δ_H 2.68 (2 H, d, *J*=6.2, CH$_2$), 3.03 (1 H, br s, OH), 4.95 (1 H, t, *J*=6.2, CHO) and 7.21-7.35 (5 H, m, ArH); δ_C 27.8 (CH$_2$), 69.8 (CO), 117.35 (C≡N), 125.45, 128.65, 128.8 and 141.0 (ArC); *m/z* 148 (M$^+$+1, <1%), 147 (M$^+$, 3), 107 (93), 79 (100), 77 (64) and 51 (20).

1-Hydroxy-1,1-diphenylacetone (4)[27]: t_r 13.50 min; ν_{max} (film) 3410 (OH), 3050, 3020, 1590, 1485 (HC=C) and 1700 cm^{-1} (C=O); δ_H 2.26 (3 H, s, Me), 4.83 (1 H, s, OH) and 7.36 (10 H, s, ArH); δ_C 26.15 (Me), 85.7 (COH), 128.0, 128.15, 128.4, 141.25 (ArC) and 208.6 (C=O); *m/z* 184 (M$^+$-42, 5%), 183 (39), 105 (100), 77 (84), 51 (17) and 43 (14).

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