Reduction of amides with $NaBH_4$ in diglyme at 162 °C

Hua-Jie Zhu, Kai-Tao Lu, Guang-Ri Sun, Jin-Bao He, Hai-Qing Li and Charles U. Pittman, Jr.

Department of Chemistry, Mississippi State University, Box 9573, Mississippi State, MS 39762, USA

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High temperature (162 °C) reductions of aromatic amides were studied to extend the useful range of functional group transformations by $NaBH_4$. Primary aromatic amides were reduced to the amines with $NaBH_4$–diglyme at 162 °C. Reduction proceeds *via* fast initial loss of hydrogen, followed by formation of the corresponding nitrile, which is then more slowly reduced to the amine. *N*-Methylbenzamide is not reduced under these conditions, but it is reduced to benzylmethylamine when LiCl is added to $NaBH_4$–diglyme at 162 °C. LiCl addition raised the rate of primary aromatic amide and aromatic nitrile conversions to both the nitrile, first, and the amine. An intermediate was isolated from the reaction of *N*-benzylformamide with $NaBH_4$–LiCl in diglyme at 162 °C. It was examined by ^1H NMR, atomic absorption, IR and thermal decomposition. Possible structures are proposed. A mechanism for the reduction of primary aromatic amides is proposed based on the initial evolution of one mole equivalent of hydrogen and formation of the nitrile prior to further reduction to amine.

The reduction of amides by hydride reagents using a variety of different metal cations and solvents is well known.[1–4] For example, $TiCl_4$–$NaBH_4$[5] or $NaBH_4$ in trifluoroacetic acid[6,7] reduce amides to amines. When used alone, $NaBH_4$ reduces aldehydes, ketones, acid chlorides, and in some cases esters, but not carboxylic acids, amides, nitriles, nitro compounds or halogenated organic molecules. Since $NaBH_4$ is safe to handle and far cheaper than more active hydride agents, such as $LiAlH_4$, $NaBEt_3H$ or $NaB(OR)_3H$, we have sought to expand the range of reductions that $NaBH_4$ can achieve by investigating its use at higher temperatures in glyme solvents.[8–10] Thus, the reductions of carboxylic acids,[8] esters,[8] nitriles,[8] benzamide,[8] 4-chlorobiphenyl[9] and pentachlorophenol[10] with $NaBH_4$ were successfully achieved at temperatures from 120–290 °C in glyme solvents. Despite the high thermal stability of $NaBH_4$, very few studies of its use in reductions at high temperatures have been carried out because it is usually used in alcohol solvents. Alcohols or other protic solvents react with $NaBH_4$ to generate hydrogen as temperature increases. Additionally, $NaBH_4$ has a very low solubility in most solvents at elevated temperatures.

We now report that aromatic primary amides are converted first to their corresponding nitriles with the evolution of one equivalent of H_2 upon treatment with $NaBH_4$ in diglyme at 162 °C. Subsequently, the nitriles are further reduced to amines under these conditions in the presence of LiCl. The nitrile conversion is very slow without LiCl present. Furthermore, evidence is presented that the reduction mechanism does not involve thermal dehydration to the nitrile nor dehydration to the corresponding imine.

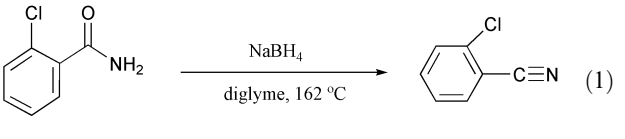
$NaBH_4$ reduction of amides in refluxing pyridine to modest yields of amines was previously reported.[11] Primary aromatic amines dehydrated to nitriles in either very low or trace yields.[11] Thus, benzamide and *p*-methoxybenzamide produced a "trace" of benzonitrile and 27% of *p*-methoxybenzonitrile, respectively, using 3 equiv. of $NaBH_4$.[11] Secondary amides were inert under these conditions and tertiary amides gave moderate yields of the corresponding tertiary amines.[11] Herein, we now demonstrate that secondary aromatic amides can be reduced to amines in moderate yields in $NaBH_4$–diglyme at 162 °C in the presence of LiCl. Furthermore, we show that LiCl addition enhances the rate of primary amide reduction by speeding the reduction of the intermediate nitrile.

Ellzey *et al.*[12] obtained 59% and 71% yields, respectively, of benzonitrile when attempting to reduce benzamide to benzylamine with 1.1 equiv. or a substantial excess of $NaBH_4$ in refluxing diglyme. No benzylamine was obtained. Newman and Fukunga[13] reported that "appreciable" yields of benzonitrile were obtained from reductions of benzamide by $LiAlH_4$ in THF. A mechanism, proceeding through initial deprotonation of the amide nitrogen followed by conversion to the dianion, $PhC(O^-\ Li^+)=N^-\ Li^+$, was postulated based on the evolution of 2 equiv. of H_2. Both $NaBH_4$ and $LiAlH_4$ are good hydride donors but $LiAlH_4$ is far more active. In addition, the relative roles of the Li^+ *versus* Na^+ counterions are different. Thus, simple parallels between these two reagents do not always exist. No mechanistic information is now available in the literature on amide reductions by $NaBH_4$ in refluxing diglyme.

Results and discussion

Reductions with $NaBH_4$ at 162 °C

The reduction of 2-chlorobenzamide, **1**, with $NaBH_4$ in diglyme at 162 °C produced 2-chlorobenzonitrile **2** in 2 h [entry 1, Table 1; eqn. (1)].



(1)

1 **2**

Nearly one mole of H_2 gas per mole of amide present was formed quickly (within 15 min). However, at this time only ~16% of the substrate had been converted to nitrile.

Table 1 Conversion of amides to nitriles with hydride reductants

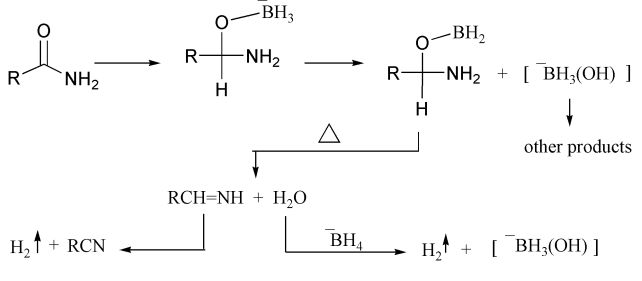
Entry	Substrate (Hydride reagent)	Hydride:substrate mole ratio	Time/h	T/°C	% Substrate consumed[a]	% Yield nitrile[b]	% Yield amine[b]
1	2-Chlorobenzamide, **1** ($NaBH_4$)	1:1	0.25	162	16	2	0
			0.5		43	40	0
			1.0		68	67	0
			2.0		86	84	0
			2.6		93	77	4
2	2-Chlorobenzamide, **1** ($LiAlH_4$)	1:1[c]	1.0	78	92	2	14
		1:1[d]	1.0	78	100	42	0
		0.6:1[d]	1.0	78	74[e]	36	1.5
3	2-Chlorobenzamide, **1** ($NaBH_4$)	1.5:1	1.0	162	37	33	0
			2.0		77	61	0
			4.0		96	63	3.4
			6.3		100	46	9
4	4-Chlorobenzamide, **6** ($NaBH_4$)	1:1	0.5	162	11	8	0
			1.0		65	60	0
			2.0		86	73	0
			3.0		99	68	0
5	4-Fluorobenzamide, **7** ($NaBH_4$)	1:1	1.0	162	83	68	0
			2.0		93	74	0
			3.3		100	64	0
6	2,2-Dimethylpropanamide, **8** ($NaBH_4$)	1.5:1:2	2.0	162	100	55	44
7	*N*-Methylbenzamide, **9** ($NaBH_4$)	1:1	2.0	162	0	–	–

[a] The calculation was based on GC analysis using a DB-5 column. [b] The yields of the nitriles and amines were obtained by GC analysis and are based on the amount of amide substrate present initially. [c] $LiAlH_4$–THF solution was injected *via* syringe into a refluxing solution of 2-chlorobenzamide in THF. [d] $LiAlH_4$–THF solution was added to the solution of 2-chlorobenzamide in THF at room temperature; the solution then was heated to reflux. [e] There are three unknown compounds (23%, 3% and 4% area percents in GC) also formed in the reaction.

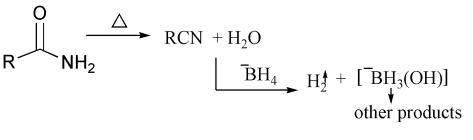
Therefore, the mechanism could not have proceeded *via* reduction of the carbonyl group to a hydroxyl function, followed by dehydration and subsequent dehydrogenation (Scheme 1). This dehydration route requires the generation of two moles of H_2 per mole of nitrile formed and needs an available proton source, which was not present in the thoroughly dried diglyme used. Simple thermal dehydration (Scheme 2) would generate one mole of water, which would rapidly give one mole of hydrogen per mole of amide consumed due to rapid reaction of that water with BH_4^- at 162 °C. However, this route requires that the generation of this hydrogen must coincide, stoichiometrically, with the consumption of amide. An equivalent of hydrogen could not be generated before an equivalent of the amide disappeared in the mechanism shown in Scheme 2. In contrast to Schemes 1 and 2, our experiments demonstrated that the mole of H_2 formed was produced long before an equivalent of the amide was consumed. Furthermore, no reaction was observed and amide **1** was recovered unchanged when **1** was heated to 162 °C in diglyme for 1 h in the absence of $NaBH_4$. Thus, borohydride must be involved in the mechanism. Finally, it is clear from entry 1 (Table 1) that substantial amounts of the substrate consumed are present as some intermediate species that is increasingly converted into products with time. All these results for $NaBH_4$ reductions in refluxing diglyme are consistent with the mechanism in Scheme 3, where **1** gives the azenolate borohydride **4** *via* **3**. Elimination *via* transition state **5** generates **2**.

$NaBH_4$ reductions of 4-chlorobenzamide, **6**, 4-fluorobenzamide, **7**, and 2,2-dimethylpropanamide, **8**, all produced the corresponding nitriles (Table 1). In contrast, the secondary amide, *N*-methylbenzamide, **9**, was inert to $NaBH_4$ in refluxing diglyme.

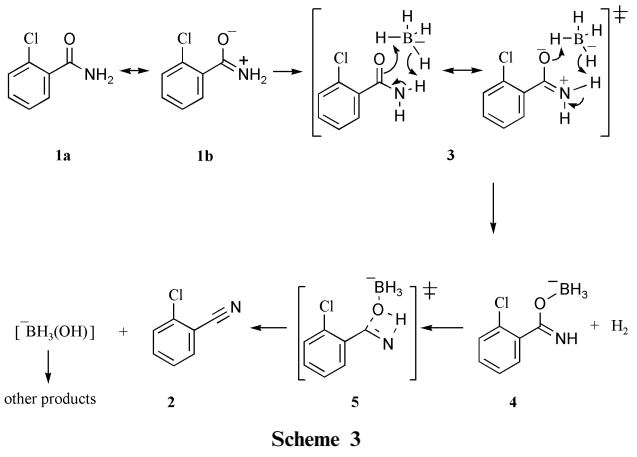
Amide **1** also reacted with $LiAlH_4$ (0.6 and 1.0 equiv.) in THF at 78 °C over 1 h to produce nitrile **2** (entry 2, Table 1). Formation of nitrile during the $LiAlH_4$ reduction of amides agrees with Newman's previous observations.[13] Only a small amount (2%) of nitrile was observed at 92% consumption of substrate **1** after 1 h using $LiAlH_4$ (1 equiv.), which had been injected as a THF solution directly into a refluxing THF solution of **1**. In this case 14% amine was formed. Addition of $LiAlH_4$ to **1** in THF at room temperature followed by heating to 78 °C produced 42% and 36% nitrile in 1 h at 100% and 74% substrate consumptions, respectively. Clearly, nitrile formation occurs prior to the reduction to amine. Furthermore, substantial amounts of an intermediate species are present at various times. In agreement with Newman's results,[13] a dehydration route is not operating. Replacing $NaBH_4$ with $LiAlH_4$ in the dehydration mechanism (shown in Scheme 2) shows that only 0.25 equiv. of $LiAlH_4$ is required to remove the 1.0 equiv. of water that would be generated per mole of amide consumed. However, about 26% of the amide substrate remained unreacted when 0.6 equiv. of $LiAlH_4$ was used (entry 2, Table 1). Taken together, these results for both $NaBH_4$ and $LiAlH_4$



Scheme 1



Scheme 2

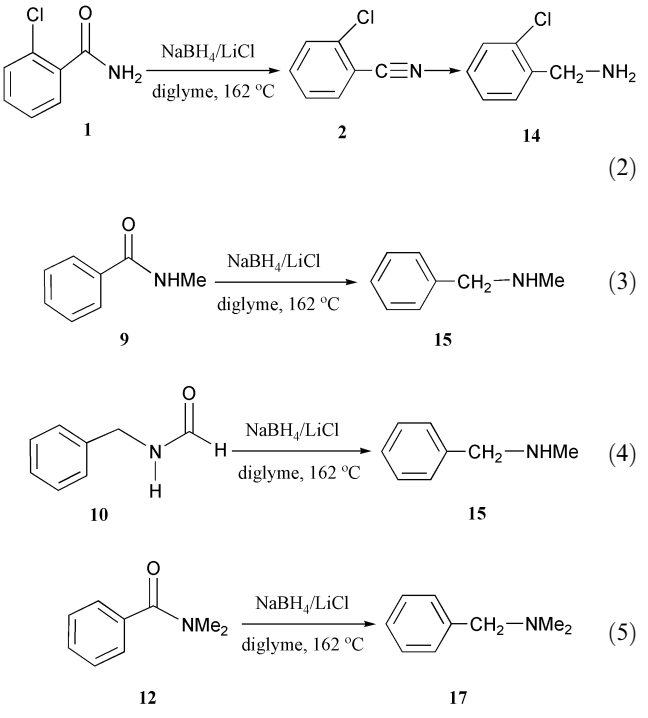


Scheme 3

rule against the dehydration mechanism during conversion of **1** to **2**. Furthermore, about two moles of H_2 was evolved using $LiAlH_4$ *versus* only one mole when $NaBH_4$ was used. This major difference is consistant with the mechanism shown in Scheme 3 for the $NaBH_4$ reductions. A different route for $LiAlH_4$ reductions is indicated by this finding [such as formation of an intermediate dianion, *o*-$ClC_6H_4C(O^-\ Li^+)=N^-\ Li^+$, originally advanced by Newman[13]].

Reduction with $NaBH_4$–LiCl at 162 °C

Addition of LiCl to the $NaBH_4$ amide reductions increased the rate of amine formation [eqns. (2)–(5), Table 2].



One equivalent of LiCl per mole of amide increased the rate of reduction of primary aryl amides, **1**, **6** and **7**, to the corresponding amines **14**, **11** and **16**, respectively (entries 1–4, Table 2). However, the nitrile was still formed first when LiCl is present (see entry 1, Table 2). Reduction of *o*-chlorobenzamide, **1**, with 1 equiv. of LiCl and $NaBH_4$ produced 55% amine in 5.5 h

Table 2 Reduction of amides with $NaBH_4$ at 162 °C in diglyme in the presence of LiCl

Entry	Substrate	$NaBH_4$:substrate:LiCl mole ratio	Time/h	% Substrate consumed[a]	% Yield nitrile[b]	% Yield amine[b]	% Isolated amine[c]
1	2-Chlorobenzamide, **1**	1:1:1	1.0	39	19	7	–
			3.0	83	32	23	
			5.5	99	16	55	
			8.0	100	11	36	
2	2-Chlorobenzamide, **1**	1.5:1:2	2.0	100	18	37	41
			4.0	100	2	46	
3	4-Fluorobenzamide, **7**	1.5:1:2	2.0	94	30	6	53
			4.0	97	21	43	
			6.0	100	1	69	
4	4-Chlorobenzamide, **6**	1.5:1:2	2.0	100	7	62	59
			4.0	100	1	64	
5	*N*-Methylbenzamide, **9**	1.5:1:1	6	59	0	52	52
			10	64	0	53	
6	*N*-Methylbenzamide, **9**	1.5:1:2	2	32	0	19	–
			9	51	0	38	
7	*N*-Benzylformamide, **10**	1.5:1:1	1.5	51	0	38	–
			3.5	55	0	55	
			6.0	55	0	34	
8	*N*-Benzylformamide, **10**	1.5:1:2	2.0	62	0	50	74
			4.0	74	0	67	
			9.0	83	0	83	
9	*N*,*N*-Diethylacetamide, **23**	1:1:0	5.0	0	0	[d]	52
		1:1:1	6.0	5	0	[d]	
		1.5:1:1	5.0	19	0	[d]	
		1.5:1:2	5.0	87	0	[d]	
10	*N*,*N*-Dimethylbenzylamide, **24**	1.5:1:1	2.0	100	0	65	68
11	δ-Valerolactam, **25**	1.5:1:1	1.5	100	–	[e]	62

[a] The calculation was based on the GC analysis using a DB-5 column. [b] The yields of the nitrile and amine were based on the consumed substrate and calculated based on GC using internal standard quantitation techniques. [c] The yield was based on the consumed substrate. [d] The low boiling triethylamine was not quantitated by GLC but it could be captured by a cold trap at −78 °C. [e] Quantitation of piperidine by GLC was difficult due to the presence of an overlapping solvent degradation product.

(see entry 1, Table 2) *versus* only 9% amine in 6.3 h without LiCl (despite having 1.5 equiv. of $NaBH_4$ present; see entry 3, Table 1). Similarly, at 2 and 4 h the amine yields obtained from **1** were, respectively, 0 and 3% without LiCl *versus* 37 and 55% (isolated) when 2 equiv. of LiCl were present under identical conditions (compare entry 2, Table 2 to entry 3, Table 1). Plots of the product distributions *versus* time for all the primary amides indicated that the effect of LiCl is largely the result of speeding up the conversion of the intermediate nitrile to amine. *p*-Chlorobenzamide, **6**, and *p*-fluorobenzamide, **7**, did not give any amine formation unless LiCl was added.

LiCl is required for practical conversion of aromatic amides to their amines with $NaBH_4$ in refluxing diglyme. The presence of Li^+ ion probably enhances the rate of nitrile reduction to amine due to its Lewis acid-like coordination to the nitrile nitrogen. Furthermore, the lithium cation, which can be tightly coordinated by diglyme, may enhance BH_4^- solubility in diglyme at 162 °C. The secondary amide, *N*-methylbenzamide, **9**, remained unreacted in $NaBH_4$–refluxing diglyme. However, **9** was converted slowly to benzylmethylamine when 1 equiv. of LiCl was added (entry 5, Table 2). Adding a second equivalent of LiCl was not further beneficial (entry 6, Table 2).

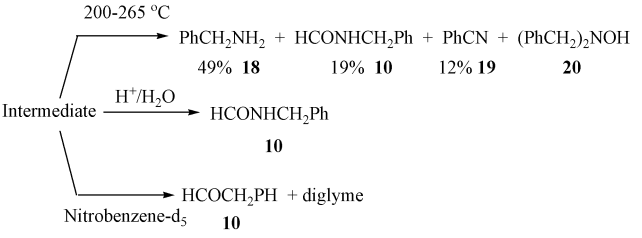
Reduction of *N*-benzylformamide with $NaBH_4$–LiCl and $LiBH_4$

The reaction of *N*-benzylformamide, **10**, with LiCl—$NaBH_4$ at 162 °C in diglyme initially produced a white solid intermediate that precipitates from the diglyme solution at 162 °C. As the reaction proceeds, benzylmethylamine, **15**, was formed slowly over 40 min. when 1 equiv. of LiCl per amide was present. The conversion of amide to the corresponding amine increased when the reaction time was extended and when the LiCl:amide mole ratio increased to 2 (entries 7 and 8, Table 2). The white solid, which initially precipitated, was isolated and thoroughly washed with fresh ether (which had been previously dried with $LiAlH_4$ and distilled directly into glassware containing the solid). Ether readily dissolves diglyme, *N*-benzylformamide, **10**, and benzylmethylamine, **15**. Thus, washing with ether was continued until no further diglyme or amide was found in the washings. Then this solid was dried at room temperature under reduced pressure (< 1 mmHg) overnight.

This isolated complex is very sensitive to moisture, decomposing when exposed to the laboratory atmosphere. The pure intermediate cannot be recrystallized from many polar and non-polar solvents, such as 1,2-dichlorobenzene, nitrobenzene, THF, DMSO benzene, hexane and so on. Other attempts were made to identify its structure. A portion of the solid was treated with 15% by wt. aqueous H_2SO_4 and the resulting solution's pH was adjusted to 10 with 15% by wt. aqueous KOH. Upon extraction with diethyl ether, diglyme and *N*-benzylformamide, **10**, in a 1:2 mole ratio were the only products detected. Amine, **15**, was not found in these products. The diglyme liberated from the solid upon treatment with H_2SO_4 must have been tightly bound in the intermediate since this solid had previously been washed many times with dried diethyl ether, a good diglyme solvent, without loss of diglyme.

The white precipitate was not formed when LiCl was absent during $NaBH_4$ reductions of **10** in diglyme at 162 °C. This strongly suggests the Li^+ ion is involved in the intermediate or promotes formation of the intermediate. Furthermore, samples of this same complex were prepared using $LiBH_4$ in place of $NaBH_4$–LiCl.

Attempts to determine the intermediate's ^{1}H NMR spectra were complicated by its extreme sensitivity to moisture and insolubility in most solvents. Nitrobenzene-d_5, dried by distillation from NaH, was finally used because the solubility of the intermediate was higher in this solvent than in solvents such as 1,2-dichlorobenzene. The ^{1}H NMR spectra of the intermediate at room temperature in nitrobenzene-d_5 exhibited a new broad singlet at 4.1 ppm for the benzylic protons and a singlet at 8.3 ppm for the proton at the carbonyl carbon. About 30% of the intermediate had also decomposed by the time the spectrum had been completed (calculated from the integration). The oxygen atoms of nitrobenzene are known to strongly coordinate with Lewis acids. Thus, the nitro group was expected to coordinate with Li^+, displacing diglyme from its coordination sites in the complex. Indeed, nitrobenzene rapidly replaced diglyme and only free diglyme was observed (3.00 ppm, s, $-OCH_3$; 3.32 ppm, t and 3.45 ppm, t, $-CH_2CH_2O-$). The resulting intermediate slowly decomposed at 25–29 °C into *N*-benzylformamide [eqn. (6)]. The diglyme:amide mole ratio determined by ^{1}H NMR integration was 0.48 and 0.50 in two separately prepared and purified samples.



(6)

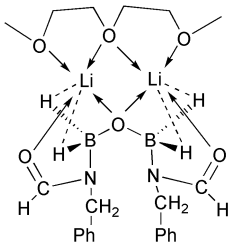
The quantity of borohydride hydrogens in the intermediate was determined by treating fresh powder samples with 15% by wt. aqueous H_2SO_4 and collecting the escaping hydrogen. The hydrogen:*N*-benzylformamide mole ratio was almost 1.9:1.0. The lithium content (3.0% by wt) and boron content is (4.6% by wt) were determined by atomic absorption. The calculated molecular weight of the intermediate is 462 or 470 based on the Li or B contents, respectively, assuming that two atoms each of Li and B are present.

Further confirmation that diglyme takes part in metal chelation in the intermediate comes from ether/diglyme exchange. The isolated intermediate was treated with dried diethyl ether and stirred strongly under dried N_2 for over 30 h and then dried *in vacuo* (< 1 mmHg) for 3 h. After > 30 h exposure of the intermediate to ether, a portion of the bound diglyme was replaced by ether. The ^{1}H NMR spectrum of this partially exchanged sample was obtained in nitrobenzene-d_5 where both ether and diglyme were displaced. The proton signals from both ethyl ether (3.07 ppm, q, *J* 6.99; 0.83 ppm, t, *J* 6.99 Hz, area ratio 2:3) and diglyme were observed. The mole ratio of ether to diglyme was ~1.1 by NMR integration.

Thermal decomposition of the complex was investigated. It decomposed into four products when heated in air to between 200 and 265 °C [eqn. (6)]. Surprisingly, benzylamine, **18**, (49%) was the major product instead of benzylmethylamine, **15**, which had been produced in the $NaBH_4$–LiCl reductions (entries 7 and 8, Table 2). Benzylamine was identified by ^{1}H NMR and mass spectrometry. Five aromatic protons at 7.2–7.4 ppm, two methylene protons at 3.9 ppm and two amino protons at 1.6 ppm constituted its ^{1}H NMR spectrum. The GC-MS (EI) spectrum exhibited a molecular ion at $m/z =$ 108 in accord with an M + 1 ion of **18** (MW 107). Its GC retention time was identical to that of authentic **18**. The second product (19%), *N*-benzylformamide, **10**, exhibited a molecular ion at $m/z = 135$ in the GC-MS (EI) and its GC retention time was the same as that of authentic **10**. Benzonitrile, **19**, (12%) was identified as the third product. The final product *N*,*N*-dibenzylhydroxyamine, **20**, (19%) was identified by GC-MS (EI) by comparing its fragmentation pattern and molecular ion ($m/z = 194$) with those of a standard *N*,*N*-dibenzylhydroxyamine spectrum.

A hypothetical structure for this species that rationalizes all of the experimental results would contain two moles of Li^+, two moles of *N*-benzylformamide, two moles of boron, and one mole of diglyme per mole of this intermediate. Two possible structures, **21** and **22**, are suggested for consideration. Both

have the empirical formula $C_{22}H_{32}N_2O_7Li_2B_2$ (4.6% B, 2.9% Li *versus* 4.6% B and 3.0% Li found by atomic absorption) and a MW of 457.6. Each would liberate 2 moles of H_2 per mole of *N*-benzylformamide present and each has a diglyme:*N*-benzylformamide mole ratio of 0.5. The NMR chemical shifts observed appear reasonable for these structures. Nevertheless, these are only postulated structures with idealized coordination of the lithium ions and one can construct related polymeric or oligomeric structures also. This species' exact structure is unknown.



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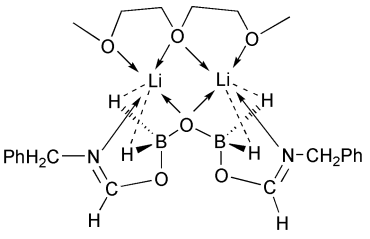

22

The successful reduction of amides to amines by $NaBH_4$ at high temperature, when added to reports of $NaBH_4$ reductions of carboxylic acids,[8] esters,[8] nitriles,[8] and chlorinated aromatic hydrocarbons[9,11] shows that this reagent can be used to reduce a wide range of functional groups (nonselectively) at high temperatures in glyme solvents.

Experimental

General

All chemicals were purchased from Aldrich Company except for diglyme, which was a gift from Ferro Corporation. ^{1}H NMR spectra were obtained on a General Electric QE-300 instrument. A Varian 3300 GC was used (DB-5, 30 meters). GC/MS were obtained on a Varian Saturn 2000 instrument. Decomposition temperatures were uncorrected.

Typical reduction procedure

2-Chlorobenzamide (155.5 mg, 1.0 mmol), LiCl (83 mg, 2.0 mmol) and the internal GC standard hexadecane (50.0 μl) were added to diglyme (10 ml) at room temperature. $NaBH_4$ (56 mg, 1.5 mmol) was added after the solution reached 162 °C and the reaction was continued for over 4 h [eqn. (1)]. The product distribution was followed *versus* time by GC analysis. Aliquots (0.2 ml) were withdrawn and treated with H_2SO_4 (15% w/w) to decompose the $NaBH_4$, followed by treatment with aqueous KOH (15% w/w) to adjust the pH of the solution to ~10. These basic solutions were extracted with ether and the products in the ether layer were analyzed by GC. After the starting material was consumed completely and most of 2-chlorobenzylnitrile was converted into 2-chlorobenzylamine, the entire reaction solution was worked up by the method described for the aliquots above. The ether solution was dried for 2 h (anhydrous Na_2SO_4) and filtered to remove Na_2SO_4. Then HCl gas was bubbled into the solution to form the hydrochloride salt of 2-chlorobenzylamine. After solvent removal *in vacuo*, the amine hydrochloride was obtained. Then it was dissolved in water and the solution pH value was adjusted to 10 with aqueous KOH. After extraction with ether (3 × 20 ml), the crude 2-chlorobenzylamine was purified by column chromatography over silica gel using ethyl acetate–hexane (1:3) elution. Pure 2-chlorobenzylamine was obtained (78 mg, 55% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.38–7.36 (2H, m), 7.35–7.33 (2H, m), 3.92 (2H, s), 1.59 (2H, br s).

The GC retention times of all products were compared with those of authentic samples by spiking experiments. The ^{1}H NMR spectra and selected MS data for other reduction products are given below.

4-Chlorobenzylamine, 11. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.31–7.22 (4H, m), 3.83 (2H, s), 1.45 (2H, s).

***N*-Methylbenzylamine, 15.** ^{1}H (300 MHz, $CDCl_3$) δ: 7.37–7.25 (5H, m), 3.75 (2H, m), 2.51 (3H, s).

4-Fluorobenzylamine, 16. ^{1}H (300 MHz, $CDCl_3$) δ: 7.29–7.25 (2H, m), 7.10–6.98 (2H, m), 3.84 (2H, s), 1.60 (2H, s).

Piperidine. ^{1}H (300 MHz, $CDCl_3$) δ: 2.80 (3H, br s), 2.10 (3H, br s), 1.53 (5H, br s).

4-Chlorobenzylnitrile. ^{1}H (300 MHz, $CDCl_3$) δ: 7.63–7.58 (2H, m), 7.50–7.45 (2H, m).

4-Fluorobenzylnitrile. ^{1}H (300 MHz, $CDCl_3$) δ: 7.71–7.66 (2H, m), 7.21–7.16 (2H, m).

2-Chlorobenzylnitrile, 2. ^{1}H (300 MHz, $CDCl_3$) δ: 7.71–7.67 (1H, m), 7.59–7.55 (2H, m), 7.45–7.37 (1H, m).

Isolated intermediate. ^{1}H NMR (300 MHz, $C_6D_5NO_2$) δ: 8.33 (1H, s), 7.19–7.04 (5H, m), 6.73 (1H, s), 4.41 (2H, d, *J* 6.10), 3.45 (2H, m), 3.43 (2H, m), 3.32 (3, s), 2.23 (1H, s). IR (KBr, cm^{-1}): 3436, 2292, 2227, 1678, 1446, 1083, 618. Atomic absorption analysis: B, 3.6%; Li, 3.0%.

Benzonitrile, 19. Produced by decomposing the intermediate. GC-MS (CI): m/z 103 (100%), 76 (52%), 50 (32%).

Benzylamine, 18. Produced by thermal decomposition of the intermediate. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.2–7.4 (5, m), 3.9 (2, s), 1.6 (2, br s). GC-MS (CI): m/z 103 (100%), 79 (50%). *N*-Benzylformamide produced by decomposing the intermediate. GC-MS (CI): m/z 135 (100%), 106 (55%), 79 (77%).

***N*,*N*-Dibenzylhydroxylamine, 20.** Produced by decomposing the intermediate. GC-MS (CI): m/z 194 (42%), 165 (2%), 117 (11%), 91 (100%), 65 (27%).

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