Russian Chemical Bulletin, International Edition, Vol. 52, No. 12, pp. 2563—2576, December, 2003

Active nickel-based reduction of organic compounds*

F. Alonso,[a] G. Radivoy,[b] and M. Yus[a]★

[a]Department of Organic Chemistry, Faculty of Sciences, Alicante University, Apdo. 99
E-03080 Alicante, Spain.**
Fax: +34 9 6590 3549. E-mail: yus@ua.es. URL: http:///www.ua.es/dept.quimorg/
[b]Department of Chemistry, Institute of Research in Organic Chemistry (INIQO), National Southern University,
1253 Alem, 8000 Bahía Blanca, Argentina.***
Fax: +54 29 1459 5187. E-mail: gradivoy@criba.edu.ar

The reducing system $NiCl_2 \cdot 2H_2O$—Li—arene$_{cat}$ (cat is catalyst) was proposed for use to reduce a wide range of organic compounds, including alkenes, alkynes, carbonyl compounds, imines, halogenated derivatives, sulfonates, aromatic compounds, hydrazines, azo and azoxy compounds, *N*-oxides, and nitrones. The degree of reduction can be controlled for some substrates. Deuterium can be incorporated in the reaction products using nickel chloride deuteriohydrate. Nitrones, *N*-alkoxyamides, and acyl azides are also reduced with the Li—arene$_{cat}$ system containing no nickel salt.

Key words: organic compounds, reduction, active metals, catalysis by arenes.

Introduction

During the last decade, new lithiation methodologies have been developed in our Department for the preparation of highly reactive organolithium intermediates based on the use of active metallic lithium. By using arenes as electron carriers, we observed that catalytic amounts of an arene, namely, naphthalene, biphenyl, or 4,4´-di-*tert*-butylbiphenyl (DTBB), can activate lithium by formation of the corresponding radical anion or dianion species, which additionally can transfer electrons to an appropriate substrate to obtain the corresponding organolithium compound.[1]

This arene-catalyzed lithiation has been applied to the preparation of organolithium compounds from non-halogenated precursors,[2] generation of polylithium intermediates,[3] and preparation of functionalized organolithium intermediates.[4] Alternatively, these reactions can be performed with polymer-supported arenes as electron carriers.[5] The Li—arene$_{cat}$ system (cat is catalyst) also found application in the activation of other metals used in reduction processes, which is the subject of the present report.

A continuous interest has been shown toward the reduction of organic compounds as a fundamental and common group transformations in synthetic organic chemistry. Among different methodologies to perform these reductions, three important general procedures can be highlighted involving the use of (a) metal hydrides, (b) dissolving metals, and (c) catalytic hydrogenation.[6a,b] Although catalytic hydrogenation is a reaction of proven efficiency,[7a,c,d] the experimental requires special care in the handling of hydrogen (a highly flammable and explosive gas) and in some cases quite expensive catalysts and/or high pressures are needed for the reaction to take place. An additional inconvenience of catalytic hydrogenation is the low control of the degree of hydrogenation of substrates containing more than one reducible group or bond.

We succeeded in discovering a new reducing system based on the activation of a transition metal by the Li—arene pair and using water as a source of hydrogen, probably the simplest one. This system is composed of nickel dichloride dihydrate obtained by the partial dehydration of the corresponding hexahydrate (Scheme 1), an excess of lithium powder, and a catalytic amount of arene (5—17 mol.%), normally naphthalene or DTBB. The general reaction conditions used are THF as a solvent and room temperature. For any of the functional groups studied, we performed four experiments, one with the abovementioned system and three blank experiments for comparison just to assure the necessity of all the components for the reaction to take place: (a) with $NiCl_2 \cdot 2H_2O$—Li (in the absence of an arene), (b) with $NiCl_2$—Li—arene$_{cat}$, and (c) with Li—arene$_{cat}$ (without the nickel salt).

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* Materials were presented at the Mark Vol´pin Memorial International Symposium "Modern Trends in Organometallic and Catalytic Chemistry" dedicated to his 80th anniversary.

** Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, E-03080 Alicante, España.

*** Instituto de Investigaciones en Química Orgánica (INIQO), Departamento de Química, Universidad Nacional del Sur, Avda Alem 1253, 8000 Bahía Blanca, Argentina.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2425—2438, December, 2003.

1066-5285/03/5212-2563 $25.00

Scheme 1

$$NiCl_2{\cdot}6H_2O \xrightarrow{i} NiCl_2{\cdot}2H_2O$$

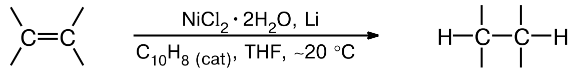
Reagents and conditions: *i*. Evacuation, 100 °C, 2 h.

Reduction of organic compounds

Reduction of alkenes. Heterogeneous or homogeneous catalytic hydrogenation is the most common method utilized for the reduction of alkenes.[6c,8] Other methodologies, in particular, those involving diimide, dissolving metals, low-valent species, or metal hydride—transition metal combinations, are of more limited application.[9]

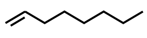
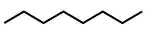
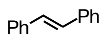
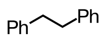
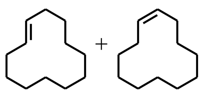
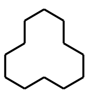
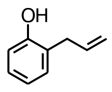
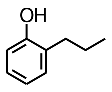
We observed that the reaction of $NiCl_2{\cdot}2H_2O$ (1.5 mmol), an excess of lithium powder (molar ratio Li : olefin = 12 : 1), and a catalytic amount of naphthalene (0.25 mmol, 17 mol.% per nickel salt) with such alkenes as oct-1-ene, *trans*-stilbene, cyclododecene, or *o*-allylphenol furnished the corresponding alkanes in excellent yields (Scheme 2, Table 1).[10,11]

Scheme 2



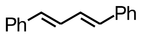
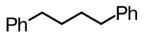
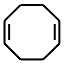
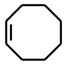
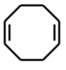
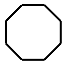
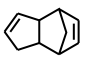
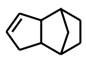
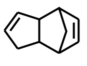
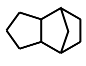
For dienes, it was possible to control the degree of reduction by adjusting the stoichiometry of the nickel salt. Thus cycloocta-1,5-diene was transformed into cyclooctene with 1.5 equiv. of nickel chloride dihydrate (see Table 2, entry *2*), whereas dicyclopentadiene underwent regioselective reduction of the carbon—carbon double bond in the six-membered ring in the presence of 1.0 equiv. of the reducing agent (see Table 2, entry *4*). In all cases, an excess of $NiCl_2{\cdot}2H_2O$ allowed the complete reduction of dienes to the corresponding alkanes (Table 2, entries *1*, *3*, and *5*).

Table 1. Reduction of alkenes[10,11]

Entry[a]	Substrate	Product	Yield (%)
1			99[b]
2			94[c]
3	 (3 : 2)		93[c]
4			97[c]

[a] The amount of $NiCl_2{\cdot}2H_2O$ was 1.5 equiv. in all experiments.
[b] GLC yield.
[c] Isolated yield after column chromatography.

Table 2. Reduction of dienes[10,11]

Entry[a]	Substrate	Amount of $NiCl_2{\cdot}2H_2O$ (equiv.)	Product	Yield (%)
1		2.5		72[a]
2		1.5		90[b]
3		2.5		96[b]
4		1.0		87[a]
5		2.5		90[a]

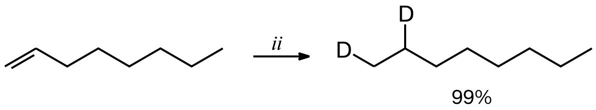
[a] Isolated yield after column chromatography.
[b] GLC yield.

A very interesting extension of this methodology is the use of nickel(II) chloride containing two molecules of deuterium oxide. This salt is prepared from anhydrous nickel chloride and excess of D_2O followed by the same thermal treatment as applied to prepare the analogous hydrate. Thus, alkenes can be transformed into dideuterioalkanes, avoiding the use of molecular deuterium (Scheme 3).

Scheme 3

$$NiCl_2 + 6D_2O \longrightarrow NiCl_2{\cdot}6D_2O$$

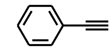
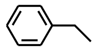
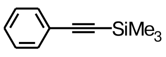
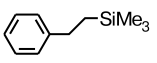
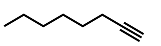
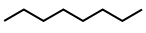
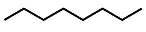
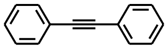
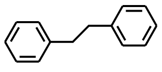
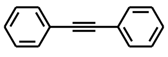
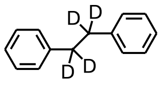
$$NiCl_2{\cdot}6D_2O \xrightarrow{i} NiCl_2{\cdot}2D_2O$$



Reagents and conditions: *i*. Evacuation, 100 °C, 2 h; *ii*. $NiCl_2{\cdot}2D_2O$, Li, $C_{10}H_{8\,(cat)}$.

Reduction of alkynes. The same general reduction methods used for alkenes are applicable to the reduction of alkynes.[6c,8,9] In general, partial reduction of alkynes is more desirable. These can be converted to *cis*- or *trans*-alkenes depending on the methodology. Catalytic hydrogenation gives predominantly *cis*-alkenes, whereas metals and metal salts give mainly *trans*-alkenes.[6d]

Table 3. Reduction of alkynes[12]

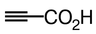
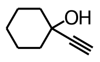
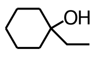
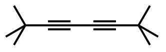
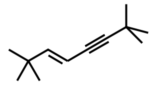
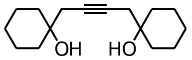
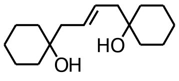
Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$ (equiv.)	Product	Yield (%)
1		2.0		70[a]
2		2.0		77[b]
3		1.0		66[a]
4		2.5		91[a]
5		2.0		85[b]
6		2.5[c]		74[b]

[a] GLC yield.

[b] Isolated yield after column chromatography.

[c] $NiCl_2 \cdot 2D_2O$ was used.

Table 4. Reduction of functionalized alkynes and semireduction of alkynes

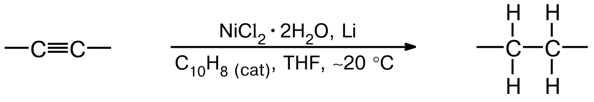
Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$ (equiv.)	Product	Yield (%)
1		2.5		90[a]
2		2.5		70[b]
3		1.0		75[a]
4		0.5		50[b]
5		1.0		72[b]

[a] GLC yield.

[b] Isolated yield after column chromatography.

When alkynes with the terminal or internal triple bond reacted with nickel(II) chloride dihydrate (2.0—2.5 mmol), an excess of lithium powder (molar ratio Li : nickel salt = 8 : 1), and a catalytic amount of naphthalene (8 mol.%), the corresponding alkanes were obtained in good to excellent yields (Scheme 4, Table 3).[12] By using the nickel salt deuteriohydrate, diphenylacetylene was transformed into 1,1,2,2-tetradeuterio-1,2-diphenylethane (see Table 3, entry *6*).

Scheme 4

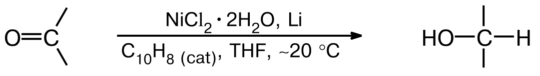


The reaction was also applied to some functionalized alkynes (Table 4, entries *1* and *2*). In some cases, the reduction can be controlled to give the corresponding *trans*-alkenes (see Table 4, entries *4* and *5*). However, when oct-4-yne was subjected to the above-mentioned system containing 1.0 equiv. of the nickel salt, the corresponding *cis*-oct-4-ene was formed after 1 h, although isomerization to *trans*-oct-4-ene was observed after longer reaction times (see Table 4, entry 3).

Reduction of carbonyl compounds and imines. Metal hydrides, dissolving metals, and catalytic hydrogenation are primarily used for the reduction of carbonyl compounds and imines. Other methods, such as electrochemical or enzymatic methods, are of less general application.[13]

By using our reducing system, we easily reduced different ketones, such as pentan-3-one, cyclohexanone, and acetophenone, to the corresponding secondary alcohols (Scheme 5, Table 5).[14] In the presence of the nickel salt deuteriohydrate, the incorporation of deuterium at position 1 of the alcohol was observed (see Table 5, entries *3* and *5*). Thus, the use of expensive metal deuterides was avoided.

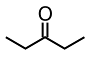
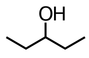
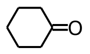
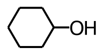
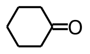
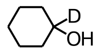
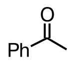
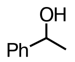
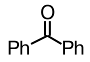
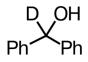
Scheme 5



Using a mixture containing 1.0 equiv. of $NiCl_2 \cdot 2H_2O$, the carbon—carbon double bond in α,β-unsatured ketones can be reduced selectively giving the corresponding saturated ketones (Table 6, entries *1* and *2*), whereas with 2.0 equiv. of $NiCl_2 \cdot 2H_2O$ complete reduction to the saturated alcohols was observed (Table 6, entries *3* and *4*). The reduction of aldehydes was not as efficient as that of ketones partially due to the competitive formation of the corresponding pinacol products under the reaction conditions employed (Table 6, entries *5*—*7*).

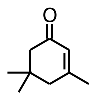
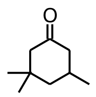
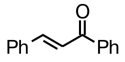
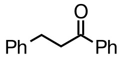
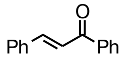
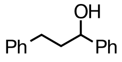
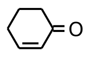
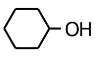
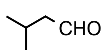
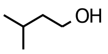
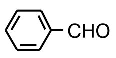
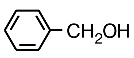
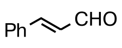
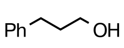
As regards imines, aldimines derived from aniline, such as isobutylidene- and benzylideneaniline, were reduced to *N*-isobutyl- and *N*-benzylaniline, respectively (Table 7, entries *1* and *2*), in the presence of naphthalene as

Table 5. Reduction of ketones[14]

Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$ (equiv.)	t/h	Product	Yield (%)
1		1.0^a	12		85^b
2		1.0^a	12		87^b
3		1.0^c	1.5		$>95^b$
4		1.0	1		75^b
5		1.0^c	3		88^d

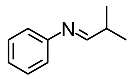
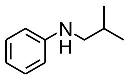
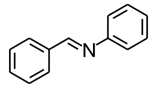
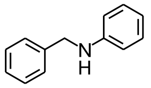
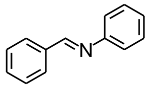
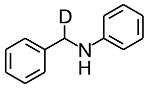
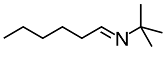
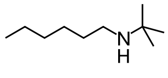
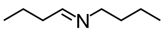
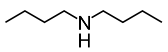
[a] At –78 °C.
[b] GLC yield.
[c] $NiCl_2 \cdot 2D_2O$ was used.
[d] Isolated yield after column chromatography.

Table 6. Reduction of carbonyl compounds[14]

Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$ (equiv.)	t/h	Product	Yield (%)
1		1.0	4		70^a
2		1.0	0.17		60^b
3		2.0	3		73^b
4		2.0	0.33		$>95^a$
5		1.0	12		58^a
6		1.0	12		64^b
7		2.0	1		54^b

[a] GLC yield.
[b] Isolated yield after column chromatography.

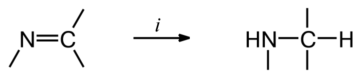
Table 7. Reduction of aldimines[14]

Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$ (equiv.)	t/h	Product	Yield[a] (%)
1		1.0^b	1		77
2		1.5^b	12		86
3		$1.5^{c,d}$	12		75
4		1.5^c	3		81
5		1.0^c	12		78^e

[a] Isolated yield after column chromatography.
[b] Naphthalene as an electron carrier.
[c] DTBB as an electron carrier.
[d] $NiCl_2 \cdot 2D_2O$ was used.
[e] GLC yield.

a catalyst (Scheme 6).[14] However, the preparation of secondary dialkylamines, such as *N*-*tert*-butylhexylamine or dibutylamine, was better acomplished with DTBB as an electron carrier (see Table 7, entries *4* and *5*). The same protocol was applied to ketimines (Table 8). Somewhat lower yield of benzylamines was caused, probably, by partial debenzylation under the reaction conditions. When the nickel salt deuteriohydrate was used instead of the hydrate, the incorporation of deuterium at the α-position was observed for both aldimines and ketimines (see Tables 7 and 8, entry *3*).

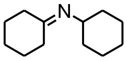
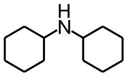
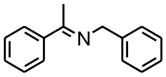
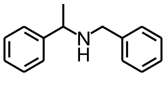
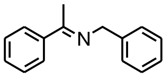
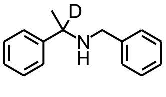
Scheme 6



Reagents and conditions: *i*. $NiCl_2 \cdot 2H_2O$, Li, THF, $C_{10}H_{8\ (cat)}$ or $DTBB_{cat}$, ~20 °C.

Hydrodehalogenation of organic halides. Chlorinated organic compounds and especially polychlorinated aromatic compounds represent a major environmental concern, because they are extremely persistent due to their slow degradation by reductive or oxidative enzymatic pathways. Therefore, efficient ways to dehalogenate these recalcitrant compounds are welcome. Numerous reagents and methods based on the use of metals have been developed for their chemical transformation into less noxious compounds.[15]

Table 8. Reduction of ketimines[14]

Entry[a]	Substrate	t/h	Product	Yield[b] (%)
1		6		78
2		3		62
3[c]		6		57

[a] The amount of $NiCl_2 \cdot 2H_2O$ was 1.5 equiv.; DTBB as an electron carrier.

[b] Isolated yield after column chromatography.

[c] $NiCl_2 \cdot 2D_2O$ is used.

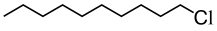
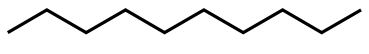
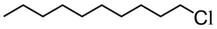
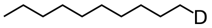
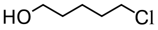
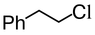
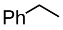
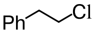
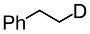
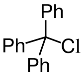
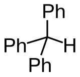
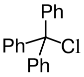
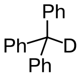
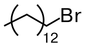
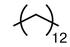
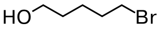
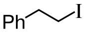
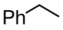
By applying our reducing system consisting of nickel(II) chloride dihydrate (molar ratio RHal : Ni^{2+} = 1 : 1), an excess of lithium powder (molar ratio Li : Ni^{2+} = 8 : 1), and a catalytic amount of DTBB (0.1 mol per 1 mol of nickel salt, 10 mol.% per nickel salt) in THF at room temperature, we reduced different alkyl chlorides, bromides, and even iodides to the corresponding alkanes (Scheme 7, Table 9).[16] When $NiCl_2 \cdot 2D_2O$ was used instead of the corresponding dihydrate, the expected deuterium-labeled compounds were obtained (Table 9, entries *2*, *5*, and *7*). It is worthy to note that fluorinated substrates (for instance, 1-fluorononane) are inert to this dehalogenation procedure.

Scheme 7

$$\mathrm{RHal} \xrightarrow[\mathrm{DTBB_{cat}},\ \mathrm{THF},\ \sim 20\ ^{\circ}\mathrm{C}]{\mathrm{NiCl_2 \cdot 2H_2O,\ Li}} \mathrm{RH}$$

More interesting from the environmental point of view was the reduction of chlorinated aromatics, such as *p*-chlorobenzyl alcohol, *p*-chlorophenol, and *p*-chloroaniline (Table 10, entries *1*, *2*, and *4*). Even the polychlorinated compound (3,5-dichlorophenol) was completely dechlorinated in excellent both GLC and isolated yields (see Table 10, entry *3*). Good results were also obtained for *p*-brominated toluene and biphenyl (see Table 10, entries *5* and *6*). The latter is a close relative of noxious polybrominated biphenyls.

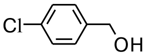
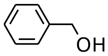
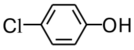
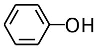
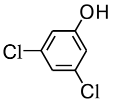
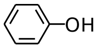
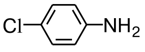
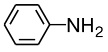
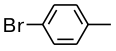
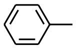
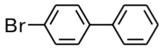
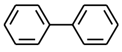
Table 9. Reduction of halogenated aliphatic compounds[16]

Entry	Substrate	Product	Yield (%)[a]
1			80 (55)
2[b]			98 (53)
3			98 (51)
4			99 (50)
5[b]			99 (56)
6			94 (66)
7[b]			93 (60)
8			99 (75)
9			98 (57)
10			89 (54)

[a] GLC yield, isolated yield is given in parentheses.

[b] $NiCl_2 \cdot 2D_2O$ was used.

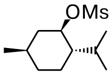
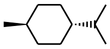
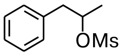
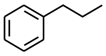
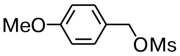
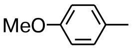
Table 10. Reduction of halogenated aromatic compounds[16]

Entry	Substrate	Product	Yield (%)*
1			84 (53)
2			98 (73)
3			99 (90)
4			92 (65)
5			99
6			89 (65)

* GLC yield; isolated yield is given in parentheses.

Reduction of sulfonates. One of the most practical methods to deoxygenate alcohols involves the transformation into their tosylates followed by the reaction with sodium iodide and final palladium-catalyzed hydrogenation or other reduction procedures.[6e,17] On the other hand, vinyl triflates can be reduced to the corresponding olefins or alkanes, and aryl triflates are reduced to arenes[18] using catalytic hydrogenation[19] or the catalytic reaction with silanes[20] or stannanes,[21] with formic acid under the palla-

Table 11. Reduction of sulfonates[24]

Entry	Substrate	Product	Yield (%)*
1	$Me(CH_2)_{10}CH_2OMs$	$Me(CH_2)_{10}Me$	85 (92)
2			72 (92)
3			72 (98)
4			73 (95)

* Isolated yield, GLC yield is given in parentheses.

dium-catalyzed conditions,[22] or with zinc and methanol in the presence of a Ni^0 catalyst.[23]

Our reduction system showed to be very efficient and versatile in the reduction of sulfonates under mild reaction conditions (Scheme 8).[24] Primary and secondary alkyl and benzyl mesylates are reduced to the corresponding alkanes in good yields (Table 11). For alkyl and aryl chlorinated mesylates, both functional groups were completely reduced (Table 12, entries *1* and *2*). The same concerns dimesylates (see Table 12, entries *3* and *4*). Alternatively, an alkyl triflate could be used as a starting material, which gave the expected deuterium-labeled product in the presence of the nickel salt deuteriohydrate (see Table 12, entry *5*).

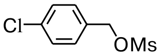
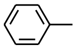
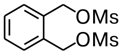
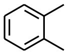
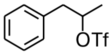
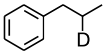
Scheme 8

$$ROSO_2R' \xrightarrow[DTBB_{cat}, \ THF, \ \sim 20 \ ^\circ C]{NiCl_2 \cdot 2H_2O, \ Li} RH$$

The versatility of our methodology was clearly demonstrated in the reduction of enol triflates. The same starting enol triflate taken in an equimolar amount with respect to the nickel salt is transformed into the corresponding alkene, while alkane is formed in the presence of an excess of the nickel salt (3 equiv.) The use of $NiCl_2 \cdot 2D_2O$ affords the deuterated vinylic compound (Table 13). Some more examples in which the reaction could be stopped at the olefin or alkane stage are shown in Table 14.

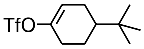
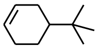
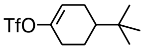
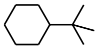
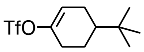
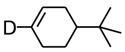
The reduction of aryl sulfonates was not so efficient. In fact, aryl mesylates failed to be reduced, whereas aryl triflates led to the expected reduced products in low yields as a result of the competitive oxygen—sulfur bond cleavage leading to the corresponding phenols (Table 15). Even considering this drawback, the method can be useful due to the easy separation of both reaction products.

Table 12. Reduction of functionalized sulfonates and triflates[24]

Entry	Substrate	Product	Yield (%)[a]
1	$ClCH_2(CH_2)_4CH_2OMs$	$Me(CH_2)_4Me$	(100)
2			43
3	$MsOCH_2(CH_2)_7CH_2OMs$	$Me(CH_2)_7Me$	70 (85)
4			57 (66)
5[b]			70

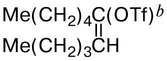
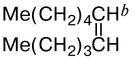
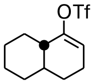
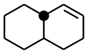
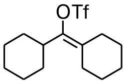
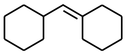
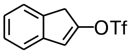
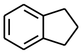
[a] Isolated yield, GLC yield is given in parentheses.
[b] $NiCl_2 \cdot 2D_2O$ was used.

Table 13. Reduction of 4-*tert*-butylcyclohexanone enol triflate[24]

Entry	Substrate	Product	Yield (%)[a]
1			58
2[b]			63
3[c]			53

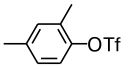
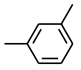
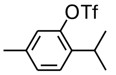
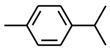
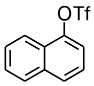
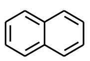
[a] Isolated yield after distillation.
[b] $NiCl_2 \cdot 2H_2O$ (3 quiv.) was used.
[c] $NiCl_2 \cdot 2D_2O$ was used.

Table 14. Reduction of other enol triflates[24]

Entry	Substrate	Product	Yield (%)[a]
1	 $Me(CH_2)_4C(OTf)^b = CH(CH_2)_3Me$	 $Me(CH_2)_4CH^b = CH(CH_2)_3Me$	68[b]
2[c]			45[d]
3			72
4			47

[a] Isolated yield.
[b] A mixture of *cis*- to *trans*-compounds (~1 : 1).
[c] $NiCl_2 \cdot 2H_2O$ (0.85 equiv.) was used.
[d] 35% of the unconsumed starting compound was recovered.

Table 15. Reduction of aryl triflates[24]

Entry	Substrate	Product	Yield (%)[a]
1			58[b] (71)
2			44[c]
3			21[d]

[a] Isolated yield; GLC yield is given in parentheses.

[b] 2,4-Dimethylphenol (15%) was also isolated.

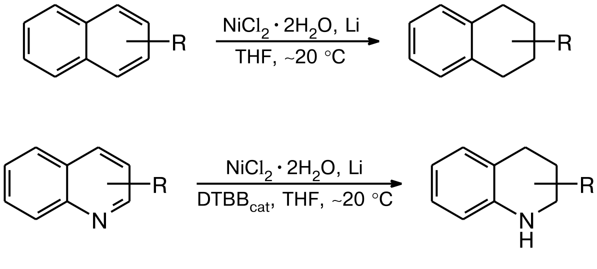
[c] 2-Isopropyl-5-methylphenol (52%) was also isolated.

[d] α-Naphthol was the main product (80%).

Reduction of aromatic compounds. Since any reduction of an aromatic system destroys the resonance stabilization and, consequently, must overcome the resonance energy, the reduction of such compounds is generally more difficult than that of alkenes, dienes, or alkynes. For example, the catalytic hydrogenation of benzene is more difficult than that of unsaturated aliphatic hydrocarbons, carbonyl compounds, nitriles, and halogen or nitro derivatives and, therefore, it is possible to reduce these functions preferentially.[6f] Probably, the most convenient method to partially reduce aromatic compounds is the so-called Birch reaction,[25,26] which makes use of alkali metals dissolving in a protic solvent, such as ammonia, primary amines or alcohols.[27] Concerning heterocyclic aromatic compounds, the selective reduction of the heterocyclic ring in benzofused systems, such as quinolines or isoquinolines, is an important transformation, because the resulting compounds are useful synthetic intermediates in the field of alkaloids.[28] In this case, a number of methods have been developed, including catalytic hydrogenation and the use of dissolving metals or boron hydrides.[28,29]

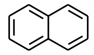
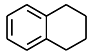
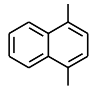
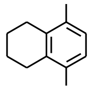
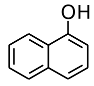
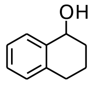
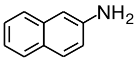
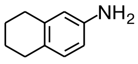
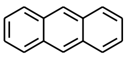
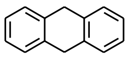
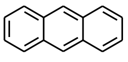
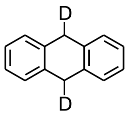
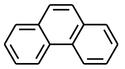
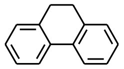
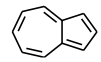
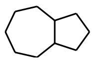
With our reducing system, we could also reduce aromatic compounds, the substrate itself acting as an electron carrier, whereas for heteroaromatic compounds the addition of a catalytic amount of DTBB was necessary for the reaction to take place (Scheme 9).

Scheme 9



For instance, the reaction of naphthalene with 3 equivalents of the nickel salt and an excess of lithium powder led to the formation of 1,2,3,4-tetrahydronaphthalene (Table 16, entry *1*).[24] The presence of different substituents in the naphthalene ring did not show any reduction pattern, since the hydroxy group (which activates the ring) led to the reduction of its own ring, whereas the methyl or amino groups led to the reduction of the other ring (see Table 16, entries *2*—*4*). In the case of anthracene, the reduction took place at the central ring, the dideuterated product being obtained when treated with the nickel salt deuteriohydrate (Table 16, entries *5* and *6*). However, a large excess of the nickel salt was needed to reduce the central ring of phenanthrene (see Table 16, entry *7*). Such a large excess allowed the total hydrogenation of azulene (a 3 : 1 diastereomeric ratio was obtained) (see Table 16, entry *8*).

Table 16. Reduction of aromatic compounds[24]

Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O$[b] (equiv.)	Product	Yield[a] (%)
1		3.0		80
2		2.5		58
3		2.0		45
4		2.0		82
5		1.5		94
6[c]		1.5		98
7		10.0		45
8		9.0		72[d]

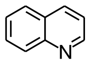
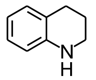
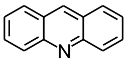
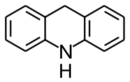
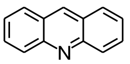
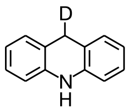
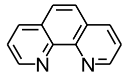
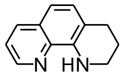
[a] Isolated yield.

[b] The substrate itself was used as an electron carrier.

[c] $NiCl_2 \cdot 2D_2O$ was used.

[d] A ~3 : 1 ratio of diastereoisomers was obtained (GLC).

Table 17. Reduction of heteroaromatic compounds[24]

Entry	Substrate	Amount of $NiCl_2 \cdot 2H_2O^b$ (equiv.)	Product	Yield[a] (%)
1		3.3		75
2		1.5		70
3[c]		1.5		73
4		1.5		57

[a] Isolated yield.

[b] DTBB was used as an electron carrier.

[c] $NiCl_2 \cdot 2D_2O$ was used.

For nitrogen-containing heteroaromatics, it was necessary to use a catalytic amount of DTBB as an electron carrier for the reaction to take place. In all cases, the reduction occurred on the nitrogenated ring.[24] Thus quinoline, acridine, and 1,10-phenanthroline were transformed into the corresponding dihydro and tetrahydro derivatives. By using the nickel salt deuteriohydrate, acridine was deuterated at position 9 (Table 17).

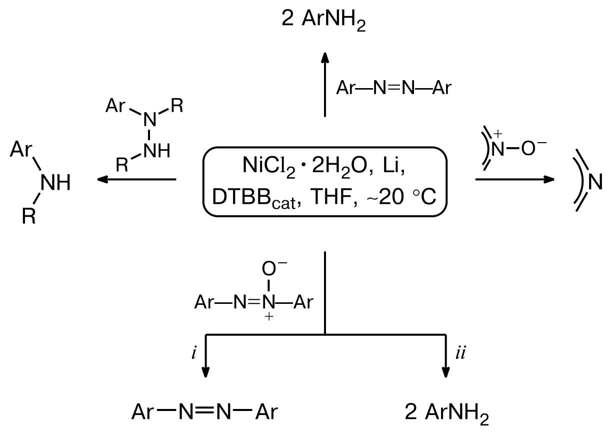
Reduction of hydrazines, azo compounds, azoxy compounds, and *N*-oxides. We studied the reduction of different nitrogen-containing functional compounds, such as hydrazines, azo and azoxy compounds, and amine *N*-oxides. There are few general methods to reduce the nitrogen—nitrogen bond in hydrazines, and the conditions required to cleave this bond depend markedly on the substituents attached to it.[30a] However, substituted hydrazines can be reduced to the corresponding amines by catalytic hydrogenation[31] or using metals in protic solvents.[32,33] The first reaction is usually carried out under pressure in an acidic medium, and in the second case, liquid ammonia is the most common solvent.

All most important methods to reduce azo compounds lead to the corresponding hydrazo derivatives.[30b,34] They include diimide, complex metal hydrides or cobalt boride in the presence of hydrazine,[7b,35] as well as metal-mediated procedures.[36—38] Concerning azoxy compounds, the corresponding deoxygenation is the most studied reaction[30c]: well-established methods include catalytic hydrogenation[39] and metal-mediated procedures.[40] In addition, azoxy compounds are cleaved to amines by potassium borohydride and copper(I) chloride.[41]

General methods[6g,30c,42] for the deoxygenation of *N*-oxides include mainly catalytic hydrogenation[43] and metal-promoted reduction.[44] The use of metal hydrides works only with boranes[45] due to possible overreduction reactions.[46]

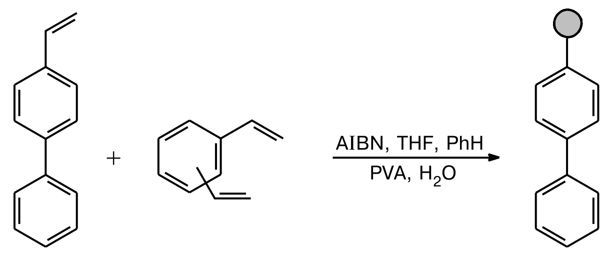
With the $NiCl_2 \cdot 2H_2O—Li—DTBB_{cat}$ system, arylhydrazines and azo compounds were reduced to anilines, azoxy compounds were reduced to azo compounds or anilines depending on the reaction conditions, and *N*-oxides were reduced to amines (Scheme 10).[47] Alternatively, some experiments were performed with a polymer-supported biphenyl as an electron carrier, prepared by the radical copolymerization of 4-vinylbiphenyl and divinylbenzene as a cross-linking agent (Scheme 11).[5,48]

Scheme 10



Conditions: *i.* 1 h; *ii.* 10 h.

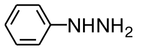
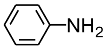
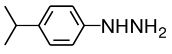
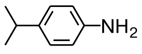
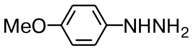
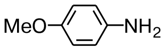
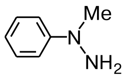
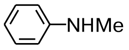
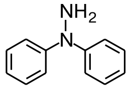
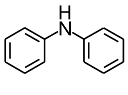
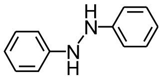
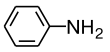
Scheme 11



PVA is poly(vinyl alcohol)

The reduction of monosubstituted and *N*,*N*- or *N*,*N*′-disubstituted hydrazines led to the formation of the corresponding primary or secondary amines (Table 18). The best results are achieved when the starting hydrazine bears at least one aryl group at one of the nitrogen atoms. Alternatively, polymer-supported biphenyl used as a catalytic electron carrier improves slightly the yield in the

Table 18. Reduction of hydrazines[47]

Entry	Substrate	Product	Yield (%)[a]
1			68
2			72
3			73
4			78 (87)[b]
5			88
6			65

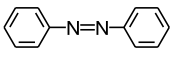
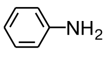
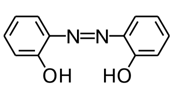
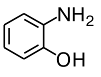
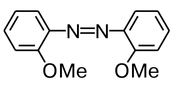
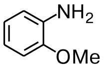
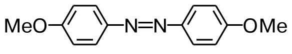
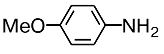
[a] Isolated yield after acid-base extraction.

[b] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

reduction of *N*-methyl-*N*-phenylhydrazine (see Table 18, entry *4*).

The application of the same procedure to azo compounds led to the corresponding anilines, and the polymer-supported biphenyl behaves similarly to DTBB (Table 19). In the case of azoxy compounds, the corresponding azo compounds were isolated for short reactions times (~1 h), whereas either longer reaction time (10 h) or 2.5 equiv. of nickel(II) chloride dihydrate led to complete reduction to the corresponding anilines (Table 20). Polymer-supported arene showed to be as efficient as DTBB (Table 20, entry *3*).

Table 19. Reduction of azo compounds[47]

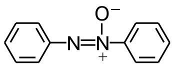
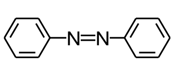
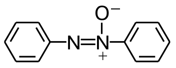
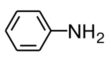
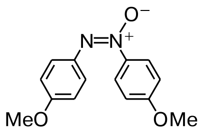
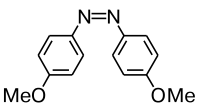
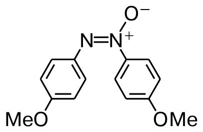
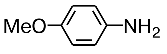
Entry	Substrate	Product[a]	Yield (%)[b]
1			70 (71)[c]
2			88
3			74
4			78

[a] The reaction mixture was kept for ~14 h with $NiCl_2 \cdot 2H_2O$ (2 equiv.).

[b] Isolated yield.

[c] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

Table 20. Reduction of azoxy compounds[47]

Entry	Substrate	Product[a]	Yield (%)[b]
1			83[c]
2			66[d]
3			79[c] (82)[e]
4			57[d]

[a] The reaction mixture was kept for ~14 h with $NiCl_2 \cdot 2H_2O$ (2 equiv.).

[b] Isolated yield.

[c] Reaction time 1 h.

[d] Reaction time 10 h.

[e] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

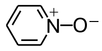
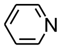
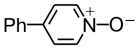
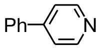
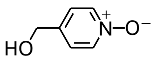
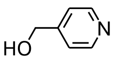
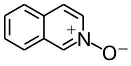
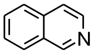
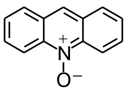
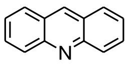
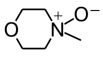
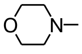
We also managed to deoxygenate a series of aromatic and one aliphatic *N*-oxide in moderate to good yields (Table 21). As in the previously mentioned cases, the reaction could also be carried out with the polymer-supported arene affording similar yields of the products.

Reduction of nitrones. Other reactions of considerable interest in organic synthesis are the deoxygenation[30c,49] and reduction[50] of nitrones. However, most of the deoxygenation methods are of limited applicability due to the harsh reaction conditions required, and practically all the literature available on the reduction of nitrones is reported in order to achieve their specific transformation into hydroxylamines. Therefore, new and alternative methodologies on these topics are welcome.

We observed that the deoxygenation of nitrones could be achieved with the Li—$DTBB_{cat}$ system in the absence of the hydrated nickel salt, whereas in its presence, further reduction to the correponding secondary amines was observed (Scheme 12).[51]

This methodology showed to be efficient in the deoxygenation of α,*N*-dialkylnitrones, cyclic nitrones, *N*-alkyl-α-arylnitrones, and a α,*N*-diarylnitrone (Table 22). Using

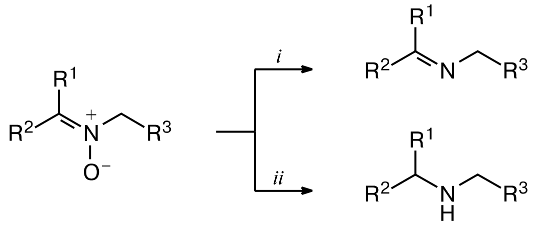
Table 21. Reduction of amine *N*-oxides[47]

Entry	Substrate	Product	Yield (%)[a]
1			68
2			66
3			55
4			70 (74)[b]
5			75
6			80

[a] Isolated yield.

[b] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

Scheme 12

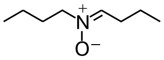
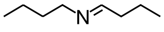
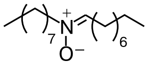
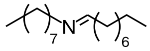
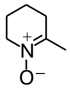
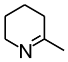
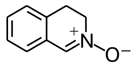
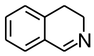
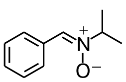
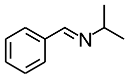
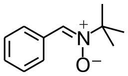
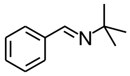
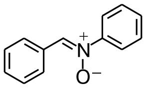
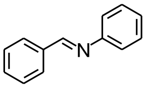


Reagents and conditions: *i*. Li, $DTBB_{cat}$, THF, ~20 °C; *ii*. $NiCl_2 \cdot 2H_2O$, Li, $DTBB_{cat}$, THF, ~20 °C.

the polymer-supported biphenyl, a slightly better yield was obtained for the deoxygenation of *N*-butyl-α-propylnitrone (Table 22, entry *1*).

In the presence of the nickel salt, a wide range of structurally different nitrones, such as cyclic α,*N*-dialkylnitrones (Table 23), as well as *N*-alkyl-α-aryl-, α,*N*-diaryl-, and *N*-benzyl-α-arylnitrones (Table 24), were directly transformed into the corresponding secondary amines. The use of the nickel salt deuteriohydrate allowed the preparation of isotopically labeled secondary amines by the incorporation of deuterium at the α-position (Table 23, entry *2* and Table 24, entry *3*). In the presence of the polymer-supported biphenyl, *N*-*tert*-butyl-α-phenylnitrone was reduced to the corresponding amine in 89% yield (see Table 24, entry *2*).

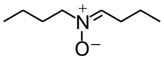
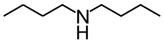
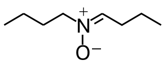
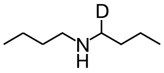
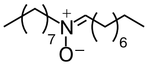
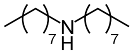
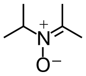
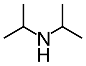
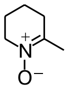
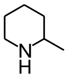
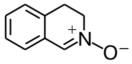
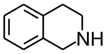
Table 22. Deoxygenation of nitrones[51]

Entry	Substrate	Product	Yield (%)[a]
1			60 (73)[b]
2			72
3			67
4			79
5			79
6			83
7			65

[a] Isolated yield after short column chromatography.

[b] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

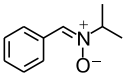
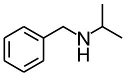
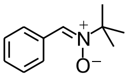
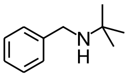
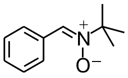
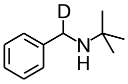
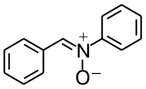
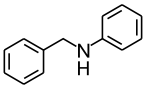
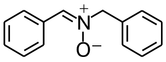
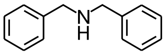
Table 23. Reduction of nitrones to amines[51]

Entry	Substrate	Product	Yield (%)[a]
1			65
2[b]			61
3			80
4			58
5			71
6			78

[a] Isolated yield after acid-base extraction.

[b] $NiCl_2 \cdot 2D_2O$ was used.

Table 24. Reduction of arylnitrones[51]

Entry	Substrate	Product	Yield (%)[a]
1			67
2			76 (89)[b]
3[c]			80
4			69
5			41

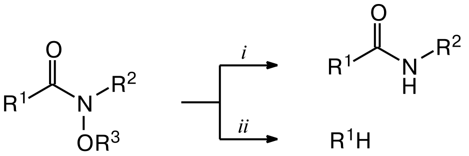
[a] Isolated yield after acid-base extraction.

[b] A vinylbiphenyl—divinylbenzene copolymer was used as an electron carrier.

[c] $NiCl_2 \cdot 2D_2O$ was used.

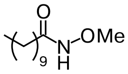
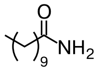
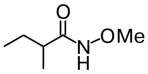
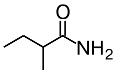
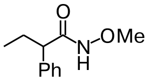
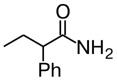
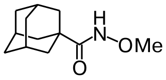
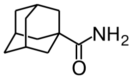
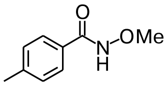
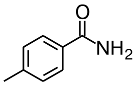
Reduction of *N*-alkoxyamides. The Weinreb amides suffer a formal reduction by demethoxylation upon exposure to lithium diisopropylamide (LDA) or *tert*-butyldimethylsilyl triflate and triethylamine by loss of formaldehyde.[52] However, the Weinreb amides with α-substituents react very slowly or not at all. Other methodologies for the reduction of the N—O bond have been developed but applied to some particular substrates only.[53] To the best of our knowledge, no work has been published on the N—O bond cleavage in secondary *N*-alkoxyamides. However, we observed that *N*-alkoxyamides could be dealkoxylated with the Li—$DTBB_{cat}$ system under very mild reaction conditions. Very surprisingly, when the reaction was performed in refluxing toluene, the corresponding alkanes were obtained from a formal dealkoxyaminocarbonylation (Scheme 13).[54]

Scheme 13



Reagents and conditions: *i*. Li, $DTBB_{cat}$, THF, −78 °C or 20 °C, 2—3 h; *ii*. Li, $DTBB_{cat}$, THF, reflux, 2 h.

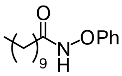
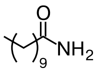
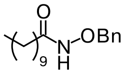
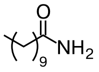
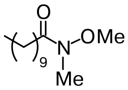
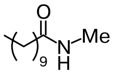
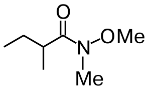
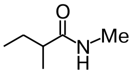
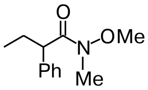
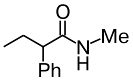
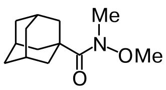
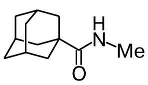
Table 25. Dealkoxylation of secondary *N*-methoxyamides[54]

Entry[a]	Substrate	Product	Yield (%)[b]
1			81
2			65
3			64
4			74
5			71

[a] The reaction was performed at −78 °C for 3 h.

[b] Isolated yield.

Table 26. Dealkoxylation of secondary *N*-alkoxyamides and the Weinreb amides[54]

Entry	Substrate	Product	Yield (%)[a]
1[b]			70
2[b]			62
3[c]			82
4[c]			88
5[c]			80
6[c]			68

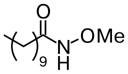
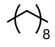
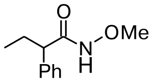
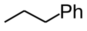
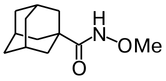
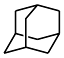
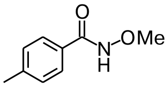
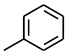
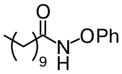
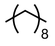
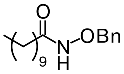
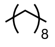
[a] Isolated yield.

[b] The reaction was performed at −78 °C for 3 h.

[c] The reaction was performed at ~20 °C for 2 h.

With an excess of lithium powder and a catalytic amount of DTBB (10 mol.%) in THF at −78 °C for 3 h, linear and branched *N*-methoxyalkane-, -cycloalkane-, and -arenecarboxamides were reduced to the corresponding primary amides (Table 25). The reaction showed to be also efficient for different *O*-substituted amides, such us

Table 27. Reduction of *N*-alkoxyamides to alkanes[54]

Entry[a]	Substrate	Product	Yield (%)[b]
1			87
2			60
3			90
4			53
5			92
6			83

[a] The reaction was performed with refluxing for 2 h.
[b] Isolated yield.

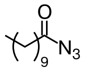
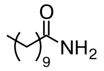
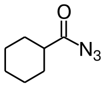
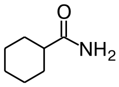
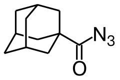
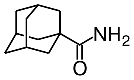
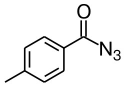
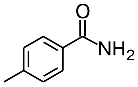
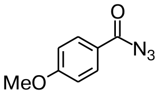
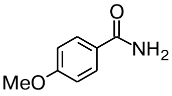
N-phenoxy- and *N*-benzyloxyamides (Table 26, entries *1* and *2*). On the other hand, the Weinreb amides underwent demethoxylation by the Li—DTBB$_{cat}$ system in 2 h at room temperature, furnishing the corresponding secondary amides in good yields (see Table 26, entries *3*—*6*).

A very interesting and unprecedent result was obtained when secondary *N*-alkoxyamides were subjected to Li—DTBB$_{cat}$ reduction in refluxing THF, yielding the corresponding alkanes (Table 27). Acyclic, cyclic, and aromatic *N*-methoxyamides, as well as *N*-phenoxy- and *N*-benzyloxyamides led to the corresponding alkanes with moderate to good yields. However, the mechanisms of these transformations remain unclear so far.

Reduction of acyl azides. Some of the published methodologies for the transformation of acyl azides into primary amides involve the use of metal borohydrides,[55] tetrathiomolybdate,[56] iodotrimethylsilane,[57] and the $NiCl_2 \cdot 6H_2O$—M (M is a transition metal)[58] or $FeCl_3$—Zn[59] systems. As an alternative to these systems, we report herein a new and simple method based on the Li—DTBB$_{cat}$ system to accomplish the reduction of acyl azides to amides.

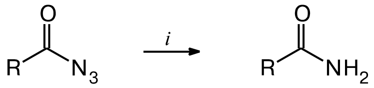
Acyl azides gave the corresponding primary amides with an excess of lithium powder (8 : 1 molar ratio of lithium to the starting compound) and a catalytic amount of DTBB (10 mol.%) in THF at room temperature for 2 h (Scheme 14). The transformation was successfully achieved for acyclic, cyclic, and aromatic acyl azides (Table 28).[54]

Table 28. Reduction of acyl azides[54]

Entry[a]	Substrate	Product	Yield (%)[b]
1			69
2			77
3			81
4			73
5			43

[a] The reaction was performed at ~20 °C for 2 h.
[b] Isolated yield.

Scheme 14

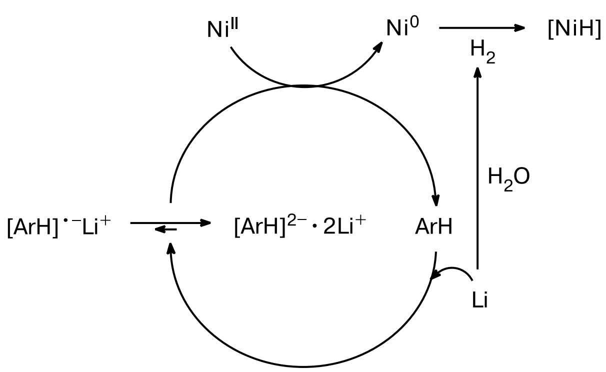


Reagents and conditions: *i*. Li, DTBB$_{cat}$, THF, ~20 °C, 2 h.

Mechanism of reactions

Concerning the use of nickel chloride dihydrate and from a mechanistic point of view, we have got some evidence that the reaction pathway can depend on the type of substrate.[60] Anyway, we have suggested a general mechanism involving two clearly different processes: (a) the reduction of Ni^{II} to Ni^0 by the Li—arene pair and

Scheme 15



(b) the generation of molecular hydrogen by the reaction of an excess of lithium with the hydration water released from the nickel salt leading to nickel hydride species (Scheme 15). Nonetheless, a dissolving-metal type mechanism or even a combination of both mechanisms must not be ruled out for certain susbtrates.

Conclusion

The $NiCl_2 \cdot 2H_2O$—Li—arene$_{cat}$ combination can be considered as an alternative and useful reducing system to attain the reduction of a wide variety of organic compounds including alkenes, alkynes, carbonyl compounds, imines, halogenated compounds, sulfonates, aromatic compounds, hydrazines, azo and azoxy compounds, *N*-oxides, and nitrones. The following advantages can be mentioned about this reducing system: (a) commercially available or easily prepared reagents are used, (b) simplicity of the procedure, since all the reagents are solid and most of the reactions are carried out at room temperature, (c) the degree of reduction can easily be controlled for many substrates, (d) easy incorporation of deuterium into the products is achieved by using the deuterated reducing system, and (e) the source of hydrogen is simply water. In the absence of the nickel salt and with the Li—arene$_{cat}$ system, nitrones, *N*-alkoxyamides, and acyl azides can also be reduced.

This work was financially supported by the General Directorate of Higher Education (DGES) of the Spanish Ministry of Education, Culture and Sports (MECD) (Grants PB97-0133 and BQU2001-0538). G. Radivoy thanks the CONICET (Buenos Aires, Argentina) for a fellowship.

References

1. (a) M. Yus, *Chem. Soc. Rev.*, 1996, **25**, 155; (b) D. J. Ramón and M. Yus, *Eur. J. Org. Chem.*, 2000, 225; (c) M. Yus, *Synlett*, 2001, 1197; (d) M. Yus, in *The Chemistry of Organolithium Compounds*, Eds. Z. Rappoport and I. Marek, Wiley, Chichester, 2003, Ch. 11.
2. D. Guijarro and M. Yus, *Recent Res. Devel. Org. Chem.*, 1998, **2**, 713.
3. F. Foubelo and M. Yus, *Trends Org. Chem.*, 1998, **7**, 1.
4. (a) C. Nájera and M. Yus, *Trends Org. Chem.*, 1991, **2**, 155; (b) C. Nájera and M. Yus, *Recent Res. Devel. Org. Chem.*, 1997, **1**, 67; (c) M. Yus and F. Foubelo, *Rev. Heteroatom Chem.*, 1997, **17**, 73; (d) C. Nájera and M. Yus, *Curr. Org. Chem.*, 2003, **7**, 867.
5. (a) C. Gómez, S. Ruiz, and M. Yus, *Tetrahedron Lett.*, 1998, **39**, 1397; (b) C. Gómez, S. Ruiz, and M. Yus, *Tetrahedron*, 1999, **55**, 7017; (c) M. Yus, C. Gómez, and P. Candela, *Tetrahedron*, 2002, **58**, 6207; (d) T. Arnauld, A. G. M. Barrett, and B. T. Hopkins, *Tetrahedron Lett.*, 2002, **43**, 1081.
6. (a) *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**; (b) M. Hudlický, *Reductions in Organic Chemistry*, American Chemical Society, Washington DC, 1996; (c) p. 53; (d) p. 57; (e) Ch. 9; (f) Ch. 6; (g) p. 131.
7. (a) P. N. Rylander, *Hydrogenation Methods*, Academic Press, London, 1985; (b) p. 168; (c) P. A. Chaloner, M. A. Esteruelas, F. Jóo, and L. A. Oro, *Homogeneous Hydrogenation*, Kluwer Academic Publishers, Dordrech, 1994; (d) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-Interscience, New York, 2001.
8. (a) S. Siegel, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**, p. 417; (b) H. Takaya, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**, p. 443.
9. D. J. Pasto, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**, p. 471.
10. F. Alonso and M. Yus, *Tetrahedron Lett.*, 1996, **37**, 6925.
11. F. Alonso and M. Yus, *J. Chem. Educ.*, 2001, **78**, 1517.
12. F. Alonso and M. Yus, *Tetrahedron Lett.*, 1997, **38**, 149.
13. *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**, Ch. 1.1—1.8.
14. F. Alonso and M. Yus, *Tetrahedron*, 1998, **54**, 1921.
15. F. Alonso, I. P. Beletskaya, and M. Yus, *Chem. Rev.*, 2002, **102**, 4009.
16. F. Alonso, G. Radivoy, and M. Yus, *Tetrahedron*, 1999, **55**, 4441.
17. Y. Ueno, C. Tanaka, and M. Okawara, *Chem. Lett.*, 1983, 795.
18. W. J. Scott and J. E. McMurry, *Acc. Chem. Res.*, 1988, **21**, 47.
19. R. P. Polniaszek and L. W. Dillard, *J. Org. Chem.*, 1992, **57**, 4103.
20. H. Kotsuki, P. K. Datta, H. Hayakawa, and H. Suenaga, *Synthesis*, 1995, 1348.
21. (a) L. A. Paquette, C. S. Ra, and S. D. Edmonson, *J. Org. Chem.*, 1990, **55**, 2443; (b) B. Dupre and A. I. Meyers, *J. Org. Chem.*, 1991, **56**, 3197.
22. (a) S. Cacchi, E. Morera, and G. Ortar, *Org. Synth.*, 1990, **68**, 138; (b) D. M. X. Donnelly, J.-P. Finet, P. J. Guiry, and R. M. Hutchinson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2851.
23. K. Sasaki, M. Sakai, Y. Sakakibara, and K. Takagi, *Chem. Lett.*, 1991, 2017.
24. G. Radivoy, F. Alonso, and M. Yus, *Tetrahedron*, 1999, **55**, 14479.
25. A. J. Birch, *Pure Appl. Chem.*, 1996, **68**, 553.
26. P. W. Rabideau, *Tetrahedron*, 1989, **45**, 1579.
27. K. Briner, in *Encyclopedia of Reagents for Organic Synthesis*, Ed. L. A. Paquette, Wiley, Chichester, 1995, **5**, p. 3003.
28. A. R. Katritzky, S. Rachwal, and B. Rachwal, *Tetrahedron*, 1996, **52**, 15031.
29. A. Srikrishna, J. R. Reddy, and R. Viswajanani, *Tetrahedron*, 1996, **52**, 1631.
30. (a) T. L. Gilchrist, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **8**, p. 388; (b) p. 382; (c) p. 390.
31. (a) A. Alexakis, N. Lensen, and P. Mangeney, *Tetrahedron Lett.*, 1991, **32**, 1171; (b) A. Alexakis, N. Lensen, and P. Mangeney, *Synlett*, 1991, 625.

32. (a) I. M. Mallor and N. M. Smith, *J. Chem. Soc., Perkin Trans 1*, 1984, 2927; (b) S. E. Denmark, O. Nicaise, and J. P. Edwards, *J. Org. Chem.*, 1990, **55**, 6219.
33. (a) M. J. Burk and J. E. Feaster, *J. Am. Chem. Soc.*, 1992, **114**, 6266; (b) S. Kobayashi and R. Hirabayashi, *J. Am. Chem. Soc.*, 1999, **121**, 6942.
34. (a) B. T. Newbold, in *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, Ed. S. Patai, Wiley, New York, 1975; (b) S. R. Sandler and W. Karo, in *Organic Functional Group Preparations*, Academic Press, Orlando, 1983, **1**, p. 452.
35. (a) A. Hajós, *Methoden der Organischen Chemie (Houben-Weyl)*, 1980, **IV/1d**, 1; (b) J. M. Pratt and G. Swinden, *J. Chem. Soc., Chem. Commun.*, 1969, 1321; (c) J. Lehmann, *Methoden der Organischen Chemie (Houben-Weyl)*, 1980, **IV/1c**, 482.
36. (a) K. K. Park and S. Y. Han, *Tetrahedron Lett.*, 1996, **37**, 6721; (b) M. L. Patil, G. K. Jnaneschwara, D. P. Sabde, M. K. Dongare, A. Sudalai, and V. H. Deshpande, *Tetrahedron Lett.*, 1997, **38**, 2137.
37. J. Bracht, *Methoden der Organischen Chemie (Houben-Weyl)*, 1981, **IV/1d**, 575.
38. W. Adam, J. N. Moorthy, W. M. Nau, and J. C. Scaiamo, *J. Am. Chem. Soc.*, 1997, **119**, 6749.
39. G. Belot and C. Degrand, *Tetrahedron Lett.*, 1976, **17**, 153.
40. (a) A. G. Hortmann, J. Koo, and C.-C. Yu, *J. Org. Chem.*, 1978, **43**, 2289; (b) H. Alper and M. Gopal, *J. Org. Chem.*, 1981, **46**, 2593; (c) R. Sánchez, G. Vest, W. Scott, and P. S. Engel, *J. Org. Chem.*, 1989, **54**, 4026.
41. Y. He, H. Zhao, X. Pan, and S. Wang, *Synth. Commun.*, 1989, **19**, 3047.
42. A. Albini and S. Pietra, *Heterocyclic N-Oxides*, CRC, Boca Raton, 1991.
43. E. C. Taylor, A. J. Crovetti, and N. E. Boyer, *J. Am. Chem. Soc.*, 1957, **79**, 3549; (b) J. A. Berson and T. Cohen, *J. Org. Chem.*, 1955, **20**, 1461.
44. (a) T. B. Sim, J. H. Ahn, and N. M. Yoon, *Synthesis*, 1996, 324; (b) K. P. Chary, G. H. Mohan, and D. S. Iyengar, *Chem. Lett.*, 1999, 1339; (c) D. K. Dutta and D. Konwar, *J. Chem. Res. (S)*, 1998, 266; (d) R. Balicki, *Synthesis*, 1989, 645.
45. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1956, **78**, 2582.
46. (a) G. A. Olah, M. Arvanaghi, and Y. D. Vankar, *Synthesis*, 1980, 660; (b) T. Morita, K. Kuroda, Y. Okamoto, and H. Sakurai, *Chem. Lett.*, 1981, 921.
47. F. Alonso, G. Radivoy, and M. Yus, *Tetrahedron*, 2000, **56**, 8673.
48. T. R. van den Ancker and C. L. Raston, *J. Organomet. Chem.*, 1998, **550**, 283.
49. (a) J. Hamer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473; (b) A. Jeevanamdam, C. Cartwright, and Y.-C. Ling, *Synth. Commun.*, 2000, **30**, 3153.
50. W. R. Bowman and R. J. Marmon, in *Comprehensive Organic Functional Group Transformations*, Eds. A. R. Katritzky, O. Meth-Cohn, C. W. Rees, and S. V. Ley, Elsevier Science, Oxford, 1995, **2**, p. 344.
51. G. Radivoy, F. Alonso, and M. Yus, *Synthesis*, 2001, 427.
52. (a) S. L. Graham and T. H. Scholz, *Tetrahedron Lett.*, 1990, **31**, 6269; (b) G. E. Keck, S. F. McHardy, and J. A. Murry, *Tetrahedron Lett.*, 1993, **34**, 6215.
53. (a) P. G. Mattingly and M. J. Miller, *J. Org. Chem.*, 1980, **45**, 410; (b) A. R. Ritter and M. J. Miller, *J. Org. Chem.*, 1994, **59**, 4602; (c) G. E. Keck, T. T. Wager, and S. F. McHardy, *Tetrahedron*, 1999, **55**, 11755.
54. M. Yus, G. Radivoy, and F. Alonso, *Synthesis*, 2001, 914.
55. (a) H. S. P. Rao, K. S. Reddy, K. Turnbull, and V. Borchers, *Synth. Commun.*, 1992, **22**, 1339; (b) B. C. Ranu, A. Savkar, and R. Chakraborty, *J. Org. Chem.*, 1994, **59**, 4114; (c) D. M. Krein, P. J. Sullivan, and K. Turnbull, *Tetrahedron Lett.*, 1996, **37**, 7213.
56. A. R. Ramesha, S. Bhat, and S. Chandrasekaran, *J. Org. Chem.*, 1995, **60**, 7682.
57. A. Kamal, N. Venugopal Rao, and E. Laxman, *Tetrahedron Lett.*, 1997, **38**, 6945.
58. (a) M. Baruah, A. Boruah, D. Prajapati, J. S. Sandhu, and A. C. Ghosh, *Tetrahedron Lett.*, 1996, **37**, 4559; (b) A. Boruah, M. Baruah, D. Prajapati, and J. S. Sandhu, *Synlett*, 1997, 1253.
59. D. Pathak, D. D. Laskar, D. Prajapati, and J. S. Sandhu, *Chem. Lett.*, 2000, 816.
60. (a) F. Alonso and M. Yus, *Adv. Synth. Catal.*, 2001, **343**, 188; (b) F. Alonso, P. Candela, C. Gómez, and M. Yus, *Adv. Synth. Catal.*, 2003, **345**, 275.

Received June 6, 2003;
in revised form November 20, 2003