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Reduction of Sulfonates and Aromatic Compounds with the $NiCl_2 \cdot 2H_2O$-Li-Arene (cat.) Combination†

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Abstract

A series of alkyl mesylates, dimesylates and alkyl or aryl triflates have been reduced to the corresponding hydrocarbons with nickel(II) chloride dihydrate, an excess of lithium powder and a catalytic amount of DTBB (10 mol%) in THF at room temperature. This methodology applied to enol triflates allowed the preparation of olefins or alkanes depending on the amount of the Ni(II) salt used. The reduction of different aromatic or heteroaromatic compounds under the above mentioned conditions leads to the partial or total reduction of the starting materials, the process being a reasonable alternative to the well-known Birch reaction. The use of the deuterium oxide-containing nickel(II) salt allows the simple preparation of deuterated products.

Keywords: Reduction; Sulfonates; Aromatic compounds; Nickel; Arene-catalysis

Introduction

Two standard routes are available to deoxygenate alcohols: (a) dehydration under acidic conditions followed by hydrogenation of the double bond under catalytic conditions, and (b) transformation of the hydroxy group in a good leaving group, followed by reduction of the newly formed functionality (usually a halogen).[1] These apparently long ways (at least two step processes) work better than the direct deoxygenation of alcohols, which requires high temperatures and pressures, so many hydroxy compounds do not survive such harsh treatment.[2] Concerning the mentioned (b) approach, one of the most practical methods involves the transformation of the alcohols into its tosylates, followed by reaction with sodium iodide (to give the corresponding alkyl iodide) and final palladium-catalysed hydrogenation or other reduction methodologies.[3] More sophisticated procedures involve the transformation of alcohols into isoureas,[4] thionocarbonates,[5] dithiocarbonates[6] or thiocarbonates[7] and further reduction with a silane, stannane or potassium in a protic solvent. On the other hand, vinyl and aryl triflates can be reduced to the corresponding olefins or alkanes, and arenes, respectively,[8] using a catalytic hydrogenation,[9] catalytic reaction with silanes[10] or stannanes,[11] with formic acid under palladium-catalysed conditions,[12] or zinc and methanol in the presence of a Ni(0) catalyst.[13]

† Part 5 in the series "The $NiCl_2 \cdot 2H_2O$-Li-Arene (cat.) Combination as Reducing System". For Part 4 see reference 19d.

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Since any reduction of an aromatic system destroys the resonance stabilisation, 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, catalytic hydrogenation of benzene is more difficult than that of unsaturated aliphatic hydrocarbons, carbonyl compounds, nitriles and halogen or nitro compounds, and therefore it is possible to reduce these functions preferentially.[14] Probably, the most convenient method to partially reduce aromatic compounds is the so-called Birch reaction,[15] which consists in using dissolving alkali metals in a protic solvent, such as ammonia, primary amines or alcohols.[16] Concerning heterocyclic aromatic compounds, the selective reduction of the heterocyclic ring in benzo fused systems, such as quinolines or isoquinolines, is an important transformation since the resulting compounds are useful synthetic intermediates in the field of alkaloids.[17] In this case a number of methods have been developed, including catalytic hydrogenation, dissolving metals or the use of boron hydrides.[17,18]

On the other hand, three years ago we discovered,[19a] that a combination of dihydrated nickel(II) chloride and lithium in the presence of a catalytic amount of naphthalene,[20] is a good mixture to carry out the reduction of olefins, the reaction being also applicable to the hydrogenation of alkynes,[19b] carbonyl compounds and their imine derivatives,[19c] and halogenated materials.[19d] In this paper we report the deoxygenation of sulfonates derived from alcohols, enols or phenols and explore the possibility of the mentioned combination for the reduction of aromatic or heteroaromatic compounds.

Results and discussion

1. Reduction of Sulfonates

The reaction of primary and secondary mesylates with an equimolecular amount of dihydrated nickel chloride, an excess of lithium [8:1 molar ratio, referred to the Ni(II) salt] and a catalytic amount of DTBB [0.1:1 molar ratio, referred to the Ni(II) salt] in THF at room temperature overnight, led to the formation of the corresponding hydrocarbons resulting from a sulfonyloxy/hydrogen exchange (Table 1, entries 1-4). Since the same reduction mixture can also be used for replacing halogens by hydrogen,[19d] chlorine-containing mesylates can be transformed into the corresponding hydrocarbons (Table 1, entries 5 and 6). Using the same methodology, dimesylates can be reduced under the same reaction conditions (Table 1, entries 7 and 8).

When the same process was applied to triflates instead of mesylates, the reaction worked under the same reaction conditions. As an example, and in order to prepare a deuterium-labelled derivative, 1-phenyl-2-propyl triflate was treated with nickel (II) chloride, containing two molecules of deuterium oxide, so the expected trifluoromethanesulfonyloxy/deuterium exchange occurred, giving the expected deuterated product (Table 1, entry 9).

We tried the same process with enol triflates. In this case, we could control the reduction to obtain the corresponding olefins or their saturated derivatives simply by adjusting the stoichiometry of the reaction: for equimolecular amounts of the triflate and the nickel salt the corresponding olefins were isolated (Table 1, entries 10 and 13-15), whereas with an excess of the metallic component (3 equivalents), a further reduction of the double bond occurred giving the expected alkane (Table 1, entry 11). Also for the enol triflates the deuterolysis can be carried out under the same reaction conditions (Table 1, entry 12). For a *cis/trans* mixture of

diastereoisomers in the starting enol triflate, the same diastereomeric ratio was obtained in the final olefins (Table 1, entry 13).

Table 1. Reduction of Sulfonates

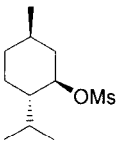
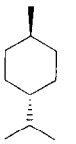
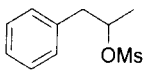
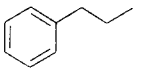
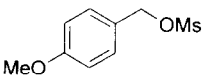
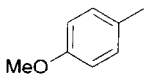
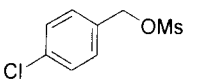
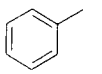
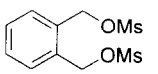
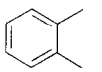
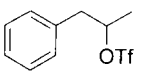
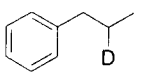
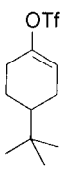
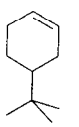
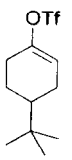
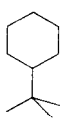
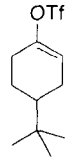
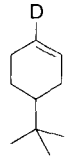
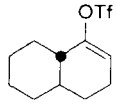
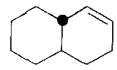
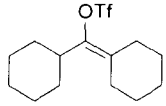
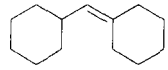
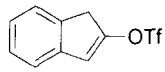
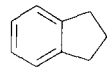
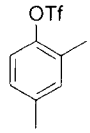
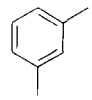
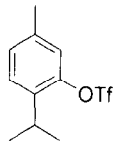
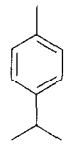
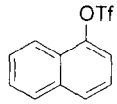
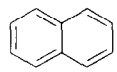
Entry	Starting material	Product[a]	Yield (%)[b]
1	$CH_3(CH_2)_{10}CH_2OMs$	$CH_3(CH_2)_{10}CH_3$	85 (92)
2			72 (92)
3			72 (98)
4			73 (95)
5	$ClCH_2(CH_2)_4CH_2OMs$	$CH_3(CH_2)_4CH_3$	(100)[c]
6			43
7	$MsOCH_2(CH_2)_7CH_2OMs$	$CH_3(CH_2)_7CH_3$	70 (85)
8			57 (66)
9[d]			70[e]
10			58[f]
11[g]			63[f]

Table 1. (cont.)

Entry	Starting material	Product[a]	Yield (%)[b]
12[d]			53[f,h]
13	$CH_3(CH_2)_4C(OTf)=CH(CH_2)_3CH_3$[i]	$CH_3(CH_2)_4CH=CH(CH_2)_3CH_3$[i]	68[i]
14[j]			45[k]
15			72
16			47
17			58[l] (71)
18			44[m]
19			17,[n] 21[o]

[a] All products were >95% pure (GLC). [b] Isolated yield after column chromatography (silica gel, hexane), unless otherwise is stated, based on the starting sulfonate. [c] Not isolated product due to its high volatility. [d] $NiCl_2{\cdot}2D_2O$ was used instead of $NiCl_2{\cdot}2H_2O$. [e] *ca.* 60% deuterium incorporation (mass spectrometry, 300 MHz ^1H NMR). [f] Purified by Kugelrohr distillation. [g] 3 Equivalents of $NiCl_2{\cdot}2H_2O$ were used. [h] *ca.* 75% deuterium incorporation (mass spectrometry, 300 MHz ^1H NMR). [i] As a *ca.* 1:1 *cis-trans* mixture (300 MHz ^1H NMR). [j] 0.85 Equivalents of $NiCl_2{\cdot}2H_2O$ were used. [k] 35% of the corresponding starting triflate was also isolated. [l] 2,4-dimethylphenol was also isolated in 15% yield. [m] 2-Isopropyl-5-methylphenol was also obtained in 52% yield. [n] α-Naphthol was the main product (80%) of the reaction. [o] Isolated yield corresponding to the reaction at reflux of THF for 4h.

Finally, since the above mentioned reaction using aryl mesylates failed, we studied the possible reduction of aryl triflates using the same methodology, finding that in this case, together with the expected reduction, involving a carbon-oxygen bond cleavage, an oxygen-sulfur bond cleavage takes place in variable amounts (Table 1, entries 17-19) giving the corresponding phenols. Even considering this drawback, the method can be useful due to the easy separation of both reaction products by acid-base extraction.

Starting alkyl mesylates[21] or alkyl and aryl triflates[22] were prepared from the corresponding hydroxy derivatives by reaction with methanesulfonyl chloride or trifluoromethanesulfonyl anhydride in the presence of a base. Starting enol triflates[23] were prepared from the corresponding carbonyl compounds by successive treatment with lithium diisopropylamide and *N*-phenyltrifluoromethanesulfonimide.

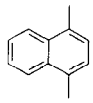
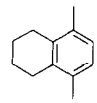
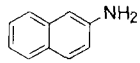
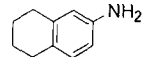
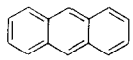
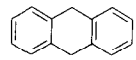
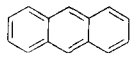
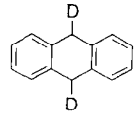
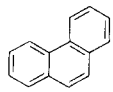
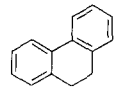
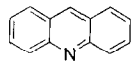
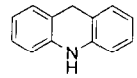
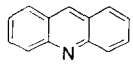
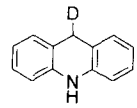
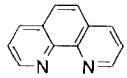
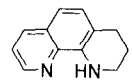
2. Reduction of Aromatic Compounds

In our ongoing study about arene-catalysed lithiations,[20,24] we have observed that in some cases, when naphthalene was used as electron carrier reagent,[25] small amounts of partially hydrogenated naphthalenes were detected after final hydrolysis with water. Thus, we decided to focus our attention on the synthetic possibilities of the reaction using for this purpose dihydrated nickel(II) chloride as the proton source as well as the transition metal catalyst.[19] The reaction of naphthalene with the mentioned salt (1:3 molar ratio) and an excess of lithium powder [1:8 molar ratio, referred to the Ni(II) salt] in THF, at ambient temperature overnight led, after filtration, to the formation of 1,2,3,4-tetrahydronaphthalene (tetralin®) (Table 2, entry 1). The existence of substituents in the starting arene does not follow any rational behaviour: the hydroxy group activates the ring leading to the reduction of its own ring (Table 2, entry 3), whereas the presence of methyl groups or amino functionality provoked the hydrogenation on the other ring (Table 2, entries 2 and 4, respectively). In the case of starting from anthracene or phenanthrene, the hydrogenation took place, as expected, at the 9,10-positions, giving the corresponding dihydroderivatives (Table 2, entries 5 and 7). For anthracene we performed the reaction using the nickel(II) salt containing deuterium oxide instead of water, so the expected dideuterio compound was isolated (Table 2, entry 6). Finally, when the standard reaction was carried out with azulene, the total hydrogenation occurred obtaining the corresponding diastereomeric mixture of saturated bicycles (Table 2, entry 8).

In the second part of this study, we considered nitrogen-containing heteroaromatics. In these cases it was necessary to use a catalytic amount [10% mol, referred to the Ni(II) salt] of DTBB as electron carrier. In all the cases considered, the hydrogenation took place on the nitrogenated ring, so starting from quinoline, acridine or 1,10-phenanthroline, the corresponding dihydro or tetrahydro compounds were isolated (Table 2, entries 9,10 and 12). Also here, acridine was deuterated at the 9-position[26] (Table 2, entry 11).

Concerning a possible mechanism for the reduction of sulfonates and aromatic compounds, and as suggested in the four previous papers on this series,[19] two pathways could be involved: (a) a dissolving metal reaction involving active metals (lithium or nickel) and a proton source (water or deuterium oxide) or (b) the generation of an active nickel(0) catalyst, which can adsorbe the hydrogen formed by reaction of the excess of lithium with water (or D_2O), working either as a catalytic hydrogenation-type reaction or involving nickel hydride species. At this moment we cannot decide which is the most probable mechanism.

Table 2. Reduction of Aromatic and Heteroaromatic Compounds

Entry	Starting material	eq. $NiCl_2 \cdot 2H_2O$[a]	Product[b]	Yield (%)[c]
1		3.0		80[d]
2		2.5		58[e]
3		2.0		45[f]
4		2.0		82[f]
5		1.5		94[d]
6[g]		1.5		98[d,h]
7		10.0		45[i]
8		9.0		72[d,j]
9		3.3[k]		75[l]
10		1.5[k]		70[m]
11[g]		1.5[k]		73[m,n]
12		1.5[k]		57[l]

[a] The substrate itself was used as electron carrier, unless otherwise is stated. [b] All products were >95% pure (GLC). [c] Isolated yields based on the starting aromatic compound. [d] Reaction crude yield, purification was not necessary. [e] Purification by column chromatography (silica gel, hexane). [f] Acid-base work-up purification. [g] $NiCl_2 \cdot 2D_2O$ was used instead of $NiCl_2 \cdot 2H_2O$. [h] For a *cis/trans* mixture see reference 13; 83% deuterium incorporation (mass spectrometry, 300 MHz ^1H NMR). [i] GLC yield; 9,10-dihydrophenanthrene was obtained together with other minor reduced compounds. [j] A *ca.* 3:1 ratio (GLC) of diastereoisomers was obtained. [k] DTBB was used as electron carrier. [l] Purification by column chromatography (silica gel, hexane/ethyl acetate). [m] Purified by crystallysation (hexane/ether). [n] >80% deuterium incorporation (mass spectrometry, 300 MHz ^1H NMR).

In conclusion, we have described here a new procedure to reduce sulfonates, which works better for alkyl mesylates and enol triflates than for aryl triflates. It can be considered an indirect way to deoxygenate alcohols, enols or phenols through the corresponding sulfonates. In the case of enol triflates the method can be used for the indirect transformation of carbonyl compounds to olefins or alkanes, depending on the stoichiometry of the reaction. We have also reported a simple way to accomplish the partial or total reduction of aromatic or heteroaromatic compounds in a Birch-type reaction, which can be of choice for the preparation of the corresponding benzo fused compounds. From a synthetic point of view, partially hydrogenated nitrogen-containing heteroaromatics are more attractive due to the structure connection with alkaloid skeletons. The use of the deuterated nickel salt allowed the easy isotopic labelling of the products.

Experimental Part

General.- For general information see references 19c and 27. All alcohols, carbonyl compounds and phenols used for the preparation of the corresponding mesylates or triflates, as well as all aromatic starting materials, were commercially available (Aldrich, Fluka) of the best grade and were used without further purification. For the preparation of dihydrated nickel (II) chloride or its deuterated derivative, see reference 19c.

Preparation of the Starting Mesylates. General Procedure.-[21] To a solution of the corresponding alcohol (2.5 mmol,) in methylene chloride (12.5 ml) containing triethylamine (1.1 ml, 4 mmol) at 0 to –10°C, was added methanesulfonyl chloride (mesyl chloride, 0.62 ml, 4 mmol) over a period of 5-10 min. Stirring for an additional 10-15 min completed the reaction. The reaction mixture was transferred to a separatory funnel with the aid of more methylene chloride (5 ml). The mixture was first extracted with ice water, followed by cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine (10 ml each). Drying of the methylene chloride solution with anhydrous Na_2SO_4, followed by solvent removal gave the mesylate, which was pure enough (GLC) for its use in reduction reactions. The following known compounds, included in Table 1, were characterised by comparison of their chromatographic and spectroscopic data (^1H and ^{13}C NMR, and MS) with those described in the literature: dodecyl methanesulfonate (entry 1),[28] (-)-menthyl methanesulfonate (entry 2),[29] 1-methyl-2-phenylethyl methanesulfonate (entry 3),[30] 4-methoxybenzyl methanesulfonate (entry 4),[31] 6-chlorohexyl methanesulfonate (entry 5),[32] 4-chlorobenzyl methanesulfonate (entry 6),[33] 9-methylsulfonyloxynonyl methanesulfonate (entry 7),[34] 2-methylsulfonyloxymethylbenzyl methanesulfonate (entry 8).[35]

Preparation of Alkyl or Aryl Triflates. General Procedure.-[22] To a solution of the corresponding alcohol or phenol (2 mmol) in pyridine (2 ml) at 0°C was slowly added trifluoromethanesulfonyl anhydride (0.38 ml, 2.3 mmol). The resulting mixture was stirred at 0°C for 5 min and then allowed to warm to room temperature and stirred for 25 h. The resulting mixture was poured into water and extracted with diethyl ether. The ether extract was washed sequentially with water, 10% hydrochloric acid solution, water, and a concentrated sodium chloride solution (2 x 10 ml each), dried (Na_2SO_4), and concentrated to yield an oil. Chromatography (flash column, hexane-ethyl acetate 20:1) afforded the corresponding 2-isopropyl-5-methylphenyl trifluoromethanesulfonate as a colorless oil. The following known compounds, included in Table 1, were characterised by comparison of their chromatographic and spectroscopic data (^1H and ^{13}C NMR, and MS) with those described

in the literature: 1-methyl-2-phenylethyl trifluoromethanesulfonate (entry 9),[36] 1-naphthyl trifluoromethanesulfonate (entry 19).[37] For new compounds, physical and spectroscopic data follow:

2,4-Dimethylphenyl Trifluoromethanesulfonate: colorless oil; t_r 8.72; ν (film) 3023, 1494, 1426, 1205, 1143, 1088, 930, 875, 820, and 737 cm^{-1}; δ_H 2.33, 2.35 (6H, 2s, 2xCH_3), and 7.03-7.14 (3H, m, ArH); δ_C 16.1, 20.6 (2xCH_3), 118.7 (q, J = 322.5, CF_3), 120.9, 128.1, 132.7, 138.3, 146.5, and 149.6 (ArC); *m/z* 254 (M^+, 33%), 122 (11), 121 (100), 93 (12), 91 (42), 77 (45), 69 (21), 65 (11), and 51 (11). HRMS calcd. for $C_9H_9F_3O_3S$ 254.0224, found 254.0225.

2-Isopropyl-5-methylphenyl Trifluoromethanesulfonate: colorless oil; t_r 9.85; ν (film) 3036, 1508, 1419, 1240, 1143, 1075, 940, 890, 841, and 765 cm^{-1}; δ_H 1.29 [6H, d, J = 6.7, $(CH_3)_2CH$], 2.38 (3H, s, CH_3Ar), 3.32 (1H, m, CH), 7.10 (1H, s, ArH), 7.19 (1H, d, J = 8.3, ArH), and 7.33 (1H, d, J = 8.3, ArH); δ_C 20.6, 23.0 (3xCH_3), 26.8 (CH), 118.7 (q, J = 320.25, CF_3), 121.5, 127.5, 129.4, 137.8, 138.0, and 147.0 (ArC); *m/z* 282 (M^+, 39%), 268 (12), 267 (100), 149 (19), 134 (42), 133 (14), 121 (28), 117 (28), 115 (22), 109 (24), 105 (32), 91 (50), 79 (15), 77 (27), 65 (13), 51 (13), and 41 (29). HRMS calcd. for $C_{11}H_{13}F_3O_3S$ 282.0537, found 282.0532.

Preparation of Enol Triflates. General Procedure.-[23] A solution of the corresponding ketone (1.0 mmol) in THF (2 ml) was added to a solution of LDA (1.1 mmol) in THF (3 ml) at –78°C, and the resultant solution was allowed to stir for 2 h. A solution of *N*-phenyltrifluoromethanesulfonimide (0.38 g, 1.07 mmol) in THF (2ml) was then added, and the reaction mixture was stirred at 0°C for 9 h. After solvent removal at the rotatory evaporator, the resultant yellow oil was purified by column chromatography on silica gel (hexane) to yield the enol triflate product. The following known compounds, included in Table 1, were characterised by comparison of their chromatographic and spectroscopic data (^1H and ^{13}C NMR, and MS) with those described in the literature: 4-*tert*-butylcyclohex-1-enyl trifluoromethanesulfonate (entry 10),[23] *trans*-3,4,4^a,5,6,7,8,8^a-octahydronaphthalen-1-yl trifluoromethanesulfonate (entry 14).[38] For new compounds, physical and spectroscopic data follow:

1H-2-Indenyl Trifluoromethanesulfonate: colorless oil; t_r 10.35; ν (film) 3080, 3020, 1616, 1421, 1219, 1135, 1085, 910, 843, and 756 cm^{-1}; δ_H 3.70 (2H, s, CH_2), 6.73 (1H, s, CH=C-O), and 7.28-7.43 (4H, m, ArH); δ_C 37.7 (CH_2), 118.7 (q, J = 321.5, CF_3), 119.5 (CH=C-O), 122.2, 123.8, 126.2, 127.3, 141.3, 147.3 (ArC), and 153.3 (CH=*C*-O); *m/z* 264 (M^+, 18%), 131 (48), 104 (11), 103 (100), 102 (19), 77 (39), 69 (18), 51 (25), and 50 (11). HRMS calcd. for $C_{10}H_7F_3O_3S$ 264.0068, found 264.0075.

(Z/E)-1-Pentyl-1-hexenyl Trifluoromethanesulfonate: colorless oil; t_r 10.38; ν (film) 3020, 1653, 1467, 1416, 1208, 1140, 1013, 932, and 904 cm^{-1}; δ_H 0.89 (12H, br s, 4xCH_3), 1.31-1.56 (20H, m, 10xCH_2), 2.02-2.40 (8H, m, 4xCH_2C=C), 5.22 (1H, t, J = 7.3, CH=C), and 5.50 (1H, t, J = 7.9, CH=C); δ_C 13.8, 13.7, 13.8 (4xCH_3), 22.1, 22.2, 22.3, 25.4, 25.9, 26.3, 29.6, 30.8, 30.9, 31.2, 33.4, 42.7 (14xCH_2), 121.1, 121.9 (2x*C*H=C), 122.6 (q, J = 321.7, CF_3), 149.1, and 150.3 (2xCH=*C*-O); *m/z* 302 (M^+, 1%), 109 (11), 99 (36), 97 (11), 96 (15), 82 (19), 81 (50), 71 (45), 69 (36), 68 (23), 67 (45), 57 (15), 56 (58), 55 (67), 54 (17), 43 (100), 42 (22), and 41 (86). HRMS calcd. for $C_{12}H_{21}F_3O_3S$ 302.1163, found 302.1162.

Cyclohexyl(cyclohexyliden)methyl Trifluoromethanesulfonate: unstable colorless oil; ν (film) 1605, 1461, 1407, 1226, 1160, 991, 890, 855, and 735 cm^{-1}; δ_H 1.19-2.59 (21H, m, 10xCH_2, CH); δ_C 26.4, 26.8, 27.0, 27.7,

28.2, 29.5, 30.0 (10xCH_2), 39.8 (CH), 122.9 (q, J = 317.3, CF_3), 131.5 (C=C-O), and 150.1 (C=C-O); *m/z* 326 (M^+, 6%), 151 (12), 111 (47), 109 (14), 95 (20), 83 (100), 81 (18), 79 (14), 69 (11), 67 (19), 55 (32), 43 (11), and 41 (22). HRMS calcd. for $C_{14}H_{21}F_3O_3S$ 326.1163, found 326.1168.

Reduction of Sulfonates with the $NiCl_2{\cdot}2H_2O$-Li-DTBB Combination. General Procedure.- To a mixture of $NiCl_2{\cdot}2H_2O$ (166 mg, 1.0 mmol) or its deuterated salt, lithium powder (56 mg, 8 mmol) and DTBB (27 mg, 0.1 mmol), was added a solution of the sulfonate (1.0 mmol) in THF (10 ml) at room temperature under an argon atmosphere. The reaction mixture, which was initially dark green, changed to black, indicating the formation of nickel(0). After total conversion of the starting material (GLC; all the reaction times were less than 10 h), the resulting suspension was diluted with ether (20 ml) and filtered off through a pad containing silica gel and celite (*ca.* 3:1). The filtrate was dried with anhydrous Na_2SO_4, evaporated (15 Torr) and the resulting residue purified as noted in Table 1. Acidic work-up with diluted HCl was employed for phenolic products. Reduced products, included in Table 1, were fully characterised by comparison of their chromatographic and spectral data with those of the corresponding commercially available pure samples [*n*-dodecane (entry 1), *n*-propylbenzene (entry 3), 4-methoxytoluene (entry 4), *n*-hexane (entry 5), toluene (entry 6), *n*-nonane (entry 7), *o*-xylene (entry 8), *t*-butylcyclohexane (entry 11), indan (entry 16), *m*-xylene (entry 17), *p*-cymene (entry 18) and naphthalene (entry 19)]. For the rest of compounds included in Table 1, literature references for all known compounds follow: *p*-menthane (entry 2),[39] 2-deuterio-1-phenylpropane (entry 9),[40] 4-*tert*-butylcyclohexene (entry 10),[41] 4-*tert*-butyl-1-deuteriocyclohexene (entry 12),[42] 5-undecene (entry 13),[43] 1,2,3,4,4a,5,6,8a-octahydronaphthalene (entry 14),[44] and 1-cyclohexylmethylenecyclohexane (entry 15).[45]

Reduction of Aromatic and Heteroaromatic Compounds using the $NiCl_2{\cdot}2H_2O$/Li-Arene Combination. General Procedure.- To a mixture of $NiCl_2{\cdot}2H_2O$ (166mg, 1.0 mmol) or its deuterated salt, lithium powder (56 mg, 8 mmol) and DTBB (27 mg, 0.1 mmol) only for heteroaromatic starting materials [in the case of aromatic substrates (Table 2, entries 1-8) it was not necessary to use DTBB because the starting material acts as electron carrier], was added a solution of the aromatic or heteroaromatic compound (1.0 mmol) in THF (10 ml) at room temperature. The reaction mixture, which was initially dark green, changed to black, indicating the formation of Ni(0). After stirring overnight, the resulting black suspension was diluted with diethyl ether (20 ml) and filtered off through a pad containing silica gel and celite (*ca.* 3:1). After drying the filtrate over anhydrous Na_2SO_4, it was evaporated (15 Torr) and the resulting residue purified as noted in Table 2. For 1-naphthol and 2-naphthylamine an acid-base work-up was used for the purification. The following compounds included in Table 2 are commercially available (Aldrich) and were characterised by comparison with authentic samples: 1,2,3,4-tetrahydronaphthalene (entry 1), 1,2,3,4-tetrahydro-1-naphthol (entry 3), 5,6,7,8-tetrahydro-2-naphthylamine (entry 4), and 1,2,3,4-tetrahydroquinoline (entry 9).

The following known compounds included in Table 2 were characterised by comparison of their chromatographic and spectroscopic data (^1H and ^{13}C NMR, and MS) with those described in the literature: 1,2,3,4-tetrahydro-5,8-dimethylnaphthalene (entry 2),[46] 9,10-dihydroanthracene (entry 5),[47] 9,10-dideuterioanthracene (entry 6),[48] 9,10-dihydrophenanthrene (entry 7),[49] perhydroazulene (entry 8),[50] 9,10-dihydroacridine (entry 10),[51] 9-deuterio-10-hydroacridine (entry 11),[52] and 1,2,3,4-tetrahydrophenanthroline (entry 12).[53]

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