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Hydrogenation of Alkynes with Hydrated Nickel Chloride, Lithium and a Catalytic Amount of Naphthalene

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Abstract: The reaction of alkynes with a mixture of nickel (II) chloride dihydrate, an excess of lithium powder and a catalytic amount of naphthalene (8 mol%) in THF at room temperature, leads to the formation of the corresponding alkanes. The incorporation of deuterium oxide into the nickel salt complex yields deuterated hydrocarbons. The process can be applied to functionalised alkynes as well as to transform alkynes into alkenes depending on the amount of the nickel salt and/or reaction times.

The most common way to reduce totally or partially carbon-carbon triple bonds is by heterogeneous[1] or homogeneous[2] catalytic hydrogenation. Other methodologies[3] avoiding the use of hydrogen include mainly the use of dissolving metal reductions,[4] low-valent metal species,[5] the combination of a hydride and a transition metal salt,[6] and in special cases the use of diimide.[7] Some inconvenients of these alternatives are: (a) Since non-conjugated olefins are in general inert to dissolving metal reductions,[8] these methods work only for the transformation of alkynes into alkenes and not for their whole reduction to alkanes; (b) Under normal reaction conditions terminal alkynes can not be reduced using dissolving metals.[9] Over the last few years we have discovered that the use of an arene as a catalyst in lithiation processes[10] allows the preparation of very reactive organolithium compounds under very mild reaction conditions. Thus, functionalised organolithium compounds[11] have been prepared by chlorine-lithium exchange[12a] or by reductive opening of saturated heterocycles;[12b] polylithiated synthons have been obtained from polychlorinated precursors.[12c] Recently we have applied this arene-catalysed lithiation to the hydrogenation of olefins in the presence of dihydrated nickel(II) chloride.[13] In the present paper we report the application of this reaction to the hydrogenation of alkynes under very mild reaction conditions.

The reaction of nickel(II) chloride dihydrate[13] (1-2.5 mmol; see Table 1), an excess of lithium powder (1: 8 molar ratio, referred to the nickel salt) and a catalytic amount of naphthalene (0.16 mmol per mmol of the nickel salt, 8 mol %) with different mono or disubstituted non-functionalised alkynes (phenylacetylene, phenyl trimethylsilylacetylene, 1-octyne, 4-octyne, diphenylacetylene) in tetrahydrofuran at room temperature gave, after stirring overnight, the corresponding alkanes (Table 1, entries 1-5). When the corresponding nickel salt contained deuterium oxide[13] instead of water, the expected tetradeuteriated product was isolated (Table 1, entry 6). Functionalised alkynes, such as propiolic acid or ethynylcyclohexanol gave the expected saturated compounds without any side-reaction (Table 1, entries 7 and 8, respectively).

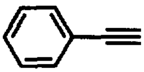
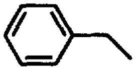
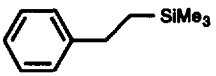
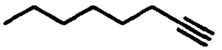
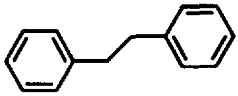
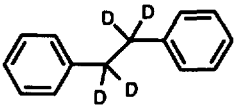
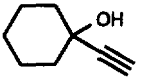
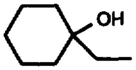
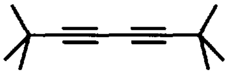
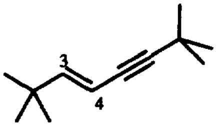
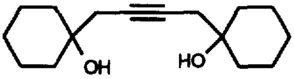
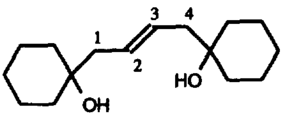
In a blank reaction, 1-ethynylcyclohexanol was submitted to the above mentioned procedure but in the absence of naphthalene: after two days at room temperature less than 5% of the corresponding product (1-ethylcyclohexanol) was detected (GLC-MS), so the role of the arene as electron carrier catalyst seems to be crucial for the reaction to proceed fast and in good yields.

Since for shorter reaction times (*ca.* 1 h), for instance in the reaction with diphenylacetylene, we found that one of the reaction products was the corresponding olefin (*E*-stilbene; GLC-MS and NMR),[14] we tried to optimise conditions for partial hydrogenation. When 4-octyne was submitted to the same reaction as above, but using 1.0 eq of the nickel salt and for 1 h, the corresponding *Z*-4-octene[15] was isolated in 75% GLC yield (Table 1, entry 9); surprisingly, for longer reaction times (overnight) a mixture of *Z/E*-4-octenes together with other octene isomers was obtained.[16] From these results it seems that the process is controlled either kinetically (short reaction time) to give the *Z*-isomer or thermodynamically (long reaction time) to give isomerisation of the initially formed *Z*-product. In fact, when 2,2,7,7-tetramethyl-3,5-octadiyne was used as starting material and using the same protocol described above (overnight) but with only 0.5 eq of the nickel salt, the corresponding *E*-enyne was obtained in 50% isolated yield:[17] this result also shows that is possible to mono-hydrogenate diynes in a stereoselective manner (Table 1, entry 10). Finally, we used the acetylenic diol[18] shown in Table 1, entry 11: in this case even with 2.0 eq of the nickel salt the corresponding *E*-enediol[19] was obtained in 75% isolated yield.

As it was commented for the hydrogenation of olefins using this methodology,[13] we think that a possible mechanism to explain the obtained results could be the sum of two processes: the reduction of Ni(II) to Ni(0) (formation of a black suspension during the reaction) and the generation of hydrogen by reaction of lithium with the water present in the nickel salt. Although no gas evolution was observed during the reaction, hydrogen could be adsorbed by the metal surface, acting so as a heterogeneous catalyst.

As a conclusion, we have shown here that the use of naphthalene-catalysed lithiation conditions in the presence of nickel(II) chloride dihydrate (or the corresponding deuteriated species) allows the full hydrogenation (or deuteration) of alkynes to the corresponding alkanes (or perdeuterioalkanes), the process being also useful for the transformation (kinetically or thermodynamically controlled) of alkynes into alkenes by modifying the reaction conditions and/or the stoichiometry of the process. It has to be pointed out that this methodology uses water as the hydrogen source.

Table1. Hydrogenation of Alkynes

Entry	Starting material	$NiCl_2.2H_2O$ eq	Product[a]	Yield (%)[b]
1		2.0		70[c]
2		2.0		77
3		1.0		66[c]
4		2.5		91[c]
5		2.0		85
6[d]		2.5		74
7		2.5		90[c]
8		2.5		70
9		1.0		75[c]
10		0.5		50
11		2.0		72

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[a] All products obtained were >95% pure (GLC and 300 MHz ^1H NMR) and were fully characterised by spectrometric means (IR, ^1H and ^{13}C NMR, and MS). [b] Isolated yield after column chromatography (silica gel, hexane/diethyl ether) based on the starting acetylene unless otherwise stated. [c] GLC yield. [d] $NiCl_2{\cdot}2D_2O$ was used instead of the corresponding dihydrated salt.

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14. The same result was observed with diphenylacetylene using $NiCl_2 \cdot 2D_2O$ as the nickel salt: after *ca.* 1 h PhCD=CDPh was detected by GLC-MS.
15. The stereochemistry of this compound was assigned by comparison with pure *Z*-4-octene (^{1}H and ^{13}C NMR), obtained by Lindlar-catalysed hydrogenation of 4-octyne (Lindlar, H.; Dubois, R. *Org. Synth. Coll. Vol. V.*; Baumgarten, H. E., Ed.; J. Wiley & Sons: New York, 1973; pp. 880-883).
16. A mixture of *Z*- (60%) and *E*-4-octene (20%) together with 2-octenes (16%) and other octenes (4%) was obtained (GLC-MS analysis).
17. The stereochemistry of this compound was assigned by ^{1}H NMR: $J_{3,4}$ = 16.2 Hz.
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19. The stereochemistry of this compound was assigned by comparison of its ^{1}H NMR data ($J_{1,2}$ = 5.2 Hz; $J_{2,4}$ = 1.55 Hz) with those of the corresponding Z-compound ($J_{1,2}$ = 4.25 Hz; $J_{2,4}$ = 1.85 Hz) prepared following the procedure described in ref 14.

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