each tube was degassed, sealed, and heated at constant temperature. After 20 h at 80 °C, the tubes were opened and the benzene solutions washed with water and analyzed by gas chromatography.

Interaction of the Nickel(I) Complex with Halogen-Containing Compounds. An authentic sample of iodotris(triethylphosphine)nickel(I) complex was prepared by mixing 25 μL of a 0.05 M THF solution of $NiI_2(PEt_3)_2$ and 25 μL of a 0.05 M THF solution of $Ni(PEt_3)_4$ with 450 μL of THF. Methyl *p*-iodobenzoate (50 μL of a 0.1 M THF solution) was added, and the mixture was degassed and sealed in a 3-mm Pyrex ESR tube. No ESR signal was observed at room temperature, but at low temperatures an intense broad singlet with a *g* value of 2.180 was observed. As the temperature was varied the line width as well as the signal intensity changed, a higher amplitude and narrower line width being observed at low temperatures. These experiments were repeated at the same temperature (−150 °C) in the presence of various halogen-containing compounds as additives.

Acknowledgment. We thank K. Rollick for assistance with the NMR experiments and the National Science Foundation for financial support.

Registry No. *trans-o*-tolylbromobis(triethylphosphine)nickel(II), 26521-33-5; *trans-o*-anisylbromobis(triethylphosphine)nickel(II), 66526-78-1; *trans*-dibromobis(triethylphosphine)nickel(II), 69460-30-6; *o*-anisyl bromide, 578-57-4; *trans-o*-anisyliodobis(triethylphosphine)nickel(II), 72111-04-7; *trans-o*-tolyliodobis(triethylphosphine)nickel(II), 59830-18-1; *trans-o*-tolylbromobis(triphenylphosphine)nickel(II), 41043-74-7; *cis*-β-bromostyrene, 588-73-8; *trans*-β-bromostyrene, 588-72-7; *cis*-β-chlorostyrene, 4604-28-8; *trans*-β-chlorostyrene, 4110-77-4; *trans-o*-tolylchlorobis(triethylphosphine)nickel(II), 28156-87-8; α-naphthyl iodide, 90-14-2; α-naphthyl bromide, 90-11-9; C_6H_5I, 591-50-4; *o*-$CH_3C_6H_4I$, 615-37-2; *p*-$CH_3C_6H_4I$, 624-31-7; *m*-$CH_3C_6H_4I$, 625-95-6; *p*-$CH_3OC_6H_4I$, 696-62-8; *p*-ClC_6H_4I, 637-87-6; C_6H_5Br, 108-86-1; *o*-$CH_3C_6H_4Br$, 95-46-5; *p*-$CH_3C_6H_4Br$, 106-38-7; *m*-$CH_3C_6H_4Br$, 591-17-3; *p*-$CH_3OC_6H_4Br$, 104-92-7; *p*-ClC_6H_4Br, 106-39-8; $Ni(PEt_3)_4$, 51320-65-1; $Ni(PPh_3)_4$, 15133-82-1; $NiBr(PEt_3)_3$, 62944-90-5; $NiBr(PPh_3)_3$, 15245-43-9; *m*-$MeOOCC_6H_4I$, 618-91-7; *p*-$MeOOCC_6H_4I$, 619-44-3; *m*-$MeOOCC_6H_4Br$, 618-89-3; *p*-$MeOOCC_6H_4Br$, 619-42-1.

Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 12.[1] New Convenient, Highly Active, and Selective Nickel Hydrogenation Catalysts

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Complex reducing agents (CRA) such as NaH–RONa–$Ni(OAc)_2$ are described as sources of new, atmospheric-pressure, heterogeneous hydrogenation catalysts. These catalysts (referred to as Nic) are cheap, easily and reproducibly prepared, not pyrophoric, and stable on long storage. They reproducibly allow highly selective semihydrogenation of alkynes to cis alkenes. Moreover, they promote the hydrogenation of alkenes. Their selectivity was exemplified by selective hydrogenations of dienes or alkene mixtures. Finally, Nic also exhibit good activity for carbonyl group hydrogenation at atmospheric pressure.

Although heterogeneous catalytic hydrogenation is a very old reaction,[2] intensive interest is still devoted to this important tool in organic synthesis.[3] Generally, the chemist calls for catalysts which are simultaneously very active and very selective, active for a large variety of functions but with a high selectivity for each group in polyfunctional substrates, very easily and reproducibly prepared, and, finally, stable on storage. If such a reagent existed, it should be an "alchemist's dream" rather than a catalyst.

With this definition in mind, it is always a challenge for the chemist to obtain a good catalyst, and numerous works have appeared on this subject.[3] Most metals have been studied, and various preparation methods have been described. Among them, reactions between transition-metal salts and reducing agents such as alkali metal/HMPA,[4] alkali metal/liquid NH_3,[5] zinc dust,[6] trialkylaluminums,[7] $LiAlH_4$,[8] or $NaBH_4$[9] have been widely used.

As part of our own research in the field of reductions, we have described the preparation of new versatile reducing systems, namely, complex reducing agents (CRA) of the type NaH–RONa–MX_n.[10] The chemical reductions performed with these reagents[11] led us to postulate metal hydrides as the reactive part of CRA. Taking into account that M–H bond formation is one of the postulated key

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[1] For part 11, see L. Mordenti, J. J. Brunet and P. Caubere, *J. Org. Chem.*, **44**, 2203 (1979). Part 12, together with ref 13, represents part of the research work of P. G. for his "these de Docteur-Ingénieur".

[2] P. Sabatier and J. B. Senderens, *C. R. Hebd. Seances Acad. Sci.*, **124**, 1358 (1897); M. Raney, U.S. Patents 1 563 587 (1927); 1 628 190 (1927); 1 915 473 (1933); A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

[3] For comprehensive books, see, for example: R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965; M. Friefelder, "Practical Catalytic Hydrogenation", Wiley-Interscience, New York, 1971.

[4] J. B. Leprince, N. Collignon, and H. Normant, *Bull. Soc. Chim. Fr.*, 367 (1976).

[5] G. W. Watt and D. D. Davies, *J. Am. Chem. Soc.*, **70**, 3753 (1948); G. W. Watt, W. F. Roper, and S. G. Parker, *ibid.*, **73**, 5791 (1951); G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 1760 (1953).

[6] See, for example: Y. Urushibara, *Bull. Chem. Soc. Jpn.*, **25**, 280 (1952); I. Motoyama, *ibid.*, **33**, 232 (1960).

[7] See, for example: Y. Takegami, T. Ueno, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **42**, 1663 (1969); R. Giezynski and S. Pasynkiewicz, *Przem. Chem.*, **52**, 746 (1973); *Organomet. Compd., Group IV Elem.*, **24**(4), i–v (1974).

[8] See, for example: Y. Takegami, T. Ueno, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **38**, 1279 (1965), and references cited therein.

[9] R. Paul, P. Buisson, and N. Joseph, *C. R. Hebd. Seances Acad. Sci.*, **232**, 627 (1951). C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003 (1963), and references cited therein. For an excellent review on $NaBH_4$ reduced Co and Ni systems, see R. C. Wade, D. G. Olah, A. N. Hughes, and b. C. Hui, *Catal. Rev.—Sci. Eng.*, **14**(2), 211 (1976).

[10] P. Caubere, *Top. Curr. Chem.*, **73**, 50 (1978), and references cited therein.

[11] J. J. Brunet, L. Mordenti, B. Loubinoux, and P. Caubere, *Tetrahedron Lett.*, 1069 (1977); J. J. Brunet, L. Mordenti, and P. Caubere, *J. Org. Chem.*, **43**, 4804 (1978); J. J. Brunet and P. Caubere, *Tetrahedron Lett.*, 3947 (1977); J. J. Brunet, R. Vanderesse, and P. Caubere, *J. Organomet. Chem.*, **157**, 125 (1978).

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steps in catalytic hydrogenations,[12] we decided to investigate CRA as sources of new hydrogenation catalysts. Our first results on nickel catalysts (referred to as Nic) have been briefly reported in a preliminary paper.[13]

In the present paper we wish to fully describe the preparation and properties of these new catalysts for *heterogeneous hydrogenations at room temperature and atmospheric pressure.*

Selective semihydrogenation of acetylenes to cis alkenes is one of the more interesting hydrogenations in organic synthesis. Thus, it was decided to first examine the behavior of Nic as regards alkynes. Satisfying results having been obtained, we then undertook the study of the more classical hydrogenation of alkenes. Finally, the possible hydrogenation of carbonyl groups at atmospheric pressure was considered.

We shall see that Nic are interesting in two ways. First, they favorably compare with the best nickel catalysts for classical selective hydrogenations, and, additionally, they allow catalytic hydrogenation of carbonyl compounds under very mild conditions. Second, their preparational concept itself opens a new field of investigation. Indeed, to the best of our knowledge, Nic are the first hydrogenation catalysts obtained from a metal salt and sodium hydride. Moreover, the activating agent needed to activate sodium hydride plays a role in the catalyst's activity, thus allowing potential modulation of its properties.

In the subsequent paper[14] we shall describe preparative-scale applications of Nic in selective hydrogenations, thus allowing evaluation of their potential usefulness in organic synthesis.

Results and Discussion

Nic Characteristics. Preparation and Physical Aspects. Nic are easily prepared by the addition of alcohol, the sodium salt of which has been chosen as activating agent, to a stirred suspension of $Ni(OAc)_2$ and a calculated excess of NaH in THF at 45 °C (see Experimental Section). After a few hours (vide infra), a mixture of Nic and a slight sodium hydride excess is obtained. When long storage is wanted, the excess sodium hydride must not be neutralized. On the contrary, this excess may be readily destroyed before use for hydrogenations (vide infra). Finally, it is easy, in special cases, to get rid of the alkoxide by simple washing with EtOH. Known quantities of catalyst may be easily syringed, after a short period of shaking, from a tank where Nic are stored under argon in the presence of the slight NaH excess. Thus, under the conditions used for the present work, 1.5 mL of the stirred suspension reproducibly corresponded to 0.5 ± 0.03 mmol of nickel (as verified more than 100 times by atomic absorption titration). Efficient centrifugation showed that the solution had no catalytic properties, thus indicating that Nic are real heterogenous catalysts. Nic themselves, obtained after neutralization of the NaH excess, are not pyrophoric, even when dry, and consitute fine, black, slightly magnetic particles about 80–90 Å in size (evaluated by X-ray and electron microscopy). After the catalyst was washed with EtOH four times and dried in a rotavapor, atomic absorption titration indicated that the resulting black powder contained 60–70% (by weight) nickel (depending on the activating alkoxide used for the preparation). This observation seems to confirm the presence of alkoxides within the insoluble framework of the catalyst.

Table I. *Influence of the Nature of Solvent on the Catalytic Hydrogenation of 1-Octyne (10 mmol) over Nic*[a, b]

solvent[c]	$t_{50\%}$,[d] min	$t_{90\%}$,[e] min
H_2O	37	57
MeOH	4.5	14.5
EtOH (abs)	10	14.5
EtOH (95%)	10.5	16.5
i-PrOH	8.5	13
$MeOCH_2CH_2OH$	11	17
AcOEt	9	13
DMF	23	32
THF	13	22
DME	11	14.5
dioxane	7	16
toluene	9	13
benzene	28	42
cyclohexane	14	18
n-hexane	17	26

[a] From *t*-AmONa as activating alkoxide, ratio of Ni/reactant of 1/20 (in moles) determined by atomic absorption after each run. [b] At 25 °C, 1 atm, and 2500 revolutions/min. [c] Volume of 15 mL. [d] Time for uptake of 10 mmol of hydrogen, i.e., 50% of the theoretical amount. [e] Time for uptake of 18 mmol of hydrogen, i.e., 90% of the theoretical amount.

Hydrogenation of Alkynes. Hydrogenation Conditions. It is well-known[15] that some care must be taken during the study of the efficiency of a catalyst. Particularly, the gas–liquid hydrogen-transfer rate may be limiting, leading to underestimating the catalytic activity.

This parameter was studied with the hydrogenation of 1-octyne to octane using conventional experimental conditions.[3,16] Nic were obtained from *t*-AmONa as activating agent. It appeared that at 4000 revolutions/min and above, the gas–liquid transfer rate was no longer limiting. However, with the very simple hydrogenation apparatus used during this study (see Experimental Section) more reproducible runs were obtained at 2500 revolutions/min. At this agitation speed, the rate of access of hydrogen to the catalyst surface was 67 cm^3/min, calculated as described by Roberts.[15] Under these conditions, the transfer of hydrogen from the gas to the liquid was not controlling, except for the more rapid hydrogenations where the gas–liquid resistance was far from negligible and did influence the observed reaction rate. However, the easily reproducible 2500 revolutions/min agitation speed was adopted and carefully monitored for each run by a stroboscope.

Influence of the Nature of the Solvent of Hydrogenation. Solvents play an important part in heterogeneous catalytic hydrogenations.[2,3] Thus, it was of interest to determine the best solvents for hydrogenations over Nic. With this intent, we chose to study the hydrogenation of 1-octyne to octane over Nic (from *t*-AmONa) in various solvents. The main results are collected in Table I. Of course, when the hydrogenation solvent was protic, the excess sodium hydride included in Nic was destroyed. When aprotic solvents were used, five drops of *t*-AmOH was added (for 0.5 mmol of Ni) just before the hydrogenation.

As may be seen from Table I, aside from ethyl acetate, dioxane, and toluene, the best solvents were found among the alcohols. Interestingly, low-polarity solvents such as

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(12) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, Academic Press, New York, 1974, p 144.

(13) J. J. Brunet, P. Gallois, and P. Caubere, *Tetrahedron Lett.*, 3955 (1977).

(14) P. Gallois, J. J. Brunet, and P. Caubere, *J. Org. Chem.*, following paper in this issue.

(15) G. W. Roberts in "Catalysis in Organic Syntheses", P. N. Rylander and H. Greenfield, Eds., Academic Press, New York, 1976.

(16) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, and references cited therein.

Table II. Influence of the Nature of the Activating Agent on the Preparation and Activity of Nic. Hydrogenation of 10 mmol of Phenylacetylene[a,b]

activating agent[c] (precursor)	prep time,[d] h	initial rate[e]
EtOH	24[f]	13.3
i-PrOH	2–3	13.4
t-BuOH	2–3	19
t-AmOH	3–4	16.7
$(Me)_3CCH_2OH$	5–6	16.7
2,5-dimethyl-2,5-hexanediol	2–3	16.7
$Et(OCH_2CH_2)_2OH$	2–3	20
C_6H_5OH	8–9	6.7

[a] Ratio of $Ni/C_6H_5C{\equiv}CH$ of 1/20 (in moles) determined by atomic absorption after each run. [b] At 25 °C (1 atm), in EtOH, and at 2500 revolutions/min. [c] NaH/ROH/$Ni(OAc)_2$ ratio of 60/20/10, except for 2,5-dimethyl-2,5-hexanediol (60/10/10). [d] Preparation time needed to reach the maximum catalyst activity. [e] Average from 0 to 20% reaction, in cubic centimeters of H_2 at STP per minute. [f] The preparation of this catalyst was poorly reproducible.

cyclohexane or *n*-hexane were found comparable to THF or 1,2-dimethoxyethane (DME). Water, DMF, and benzene were found to be poorly efficient.

It must be emphasized that during hydrogenation of 1-octyne, intermediate formation of nearly 80% 1-octene was observed, whatever the solvent (Table I). This was the first observation on the potential possibilities of semihydrogenation of alkynes over Nic.

Influence of the Nature of the Activating Alkoxide. The influence of the nature of activating alkoxide on both the preparation and the properties of Nic was briefly investigated. The alkoxides were chosen from among those tested for complex bases.[10] The data quoted in Table II refer to hydrogenation of the cheap and easily available phenylacetylene in EtOH.

As may be seen from the initial rates reported in Table II, the activating alkoxide plays a part in the activity of the corresponding Nic, thus allowing the possibility of modulation, as expected. As for complex bases,[10] EtONa was not a good activating agent. Water was also tested; the results obtained were poorly reproducible, and the preparation times were as long as 72 h. However, it is noteworthy that water may lead to Nic.

Obviously, some control experiments were performed. Thus, no catalytic activity was found either for NaH–$Ni(OAc)_2$ or for *t*-AmONa–$Ni(OAc)_2$ mixtures prepared under simulated reaction conditions. Note that the inactivity of NaH as a hydrogenation catalyst under mild conditions is well-known.[17]

It must be emphasized that intermediate formation of 90% vinylbenzene was observed during hydrogenations of phenylacetylene, thus reinforcing the idea of a possible application of Nic for selective semihydrogenations of alkynes.

Finally, it was of interest to know if Nic may be stored for a long time without too much loss of activity for the reduction of acetylenic compounds. To obtain this information, we prepared a few Nic in the usual way and stored them (with slight NaH excess) at room temperature under argon (see Experimental Section). After various durations, 1.5-mL portions (0.5 mmol of Ni) were syringed and tested for hydrogenation of phenylacetylene in EtOH.

The very high stability of Nic after 7 months of storage is evident from the data given in Table III. After 14 months we tested the stability of the Nic the most often used during our work (*t*-AmONa as activating agent). It is noteworthy that even for so long a storage time, the loss of activity was very low. (We shall see below that a good stability was also found for alkene hydrogenations.)

Table III. Effect of Storage on the Activity of Some Nic for the Hydrogenation of 10 mmol of Phenylacetylene in EtOH (15 mL)[a,b]

	effect of storage on t_{200},[c] min		
catalyst prepared from	initial	7 months	14 months
NaH–*t*-AmONa–$Ni(OAc)_2$	12	13	15
NaH–*t*-BuONa–$Ni(OAc)_2$	10.5	12	not tested
NaH–*i*-PrONa–$Ni(OAc)_2$	15	15	not tested
NaH–$Et(OCH_2CH_2)_2ONa$–$Ni(OAc)_2$	10.5	12	not tested

[a] At 25 °C, 1 atm, and 2500 revolutions/min. [b] Ratio of $Ni/C_6H_5C{\equiv}CH$ of 1/20 (in moles). [c] Time for uptake of the first 200 cm^3 of hydrogen. The exact t_{200} values were obtained after correction from the curves t_{200} vs. catalyst loading in the range 0.2–1 mmol of Ni for freshly prepared catalysts.

Table IV. Influence of the Nickel/Reactant Ratio for the Hydrogenation of 1-Octyne over Nic (0.15 mmol) in EtOH (15 mL)[a]

Ni/reactant ratio	initial rate[b]	$t_{90\%}$,[c] min
1/20	17.5	5
1/50	17.5	13
1/100	17.5	25
1/200	16.5	65

[a] At 2500 revolutions/min. [b] Average rate from 0 to 20% reaction in cubic centimeters of H_2 at STP per minute. [c] Time for uptake of 18 mmol of hydrogen, i.e., 90% of the theoretical amount.

In the above studies a Nic/reactant ratio of 1/20 was chosen for more convenient comparison with general literature data. However, it was of interest to know if a lower Nic/reactant ratio might be used. This parameter was briefly studied with the hydrogenation of 1-octyne as a reaction test. As may be seen from Table IV, Nic may be used even with a very low metal/reactant ratio. This property may be, of course, of practical interest.

Selective Semihydrogenation of Alkynes. In the above studies, it was observed that, during alkyne hydrogenations, relatively little formation of alkane occurred until most of the alkyne had been converted into alkene, even when the further hydrogenation of the alkene was the faster reaction. Such an observation has already been noted in the literature and accounted for by the preferential complexation of an alkyne relative to an alkene over the catalyst.[18] To test the potential capability of Nic for selective semihydrogenation of alkynes, hydrogenation of representative substrates was performed (Table V).

These data show without ambiguity that Nic are very promising catalysts for selective semihydrogenation of alkynes. (It must be noted that, in some cases, the gas-liquid hydrogen transfer was far from negligible.) However, such simple data do not give a true view of the hydrogenation progression. Thus, for a more comprehensive understanding of the process, the complete pathway followed by a mono- and a disubstituted alkyne (namely, 1-octyne and 2-hexyne) during their complete hydrogenation was studied (Figures 1 and 2) by GLC analysis of

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(17) L. H. Slaugh, *J. Org. Chem.*, **32**, 108 (1967).

(18) R. J. Card, C. E. Liesner, and D. C. Neckers, *J. Org. Chem.*, **44**, 1095 (1979), and references cited therein.

Table V. Semihydrogenation of Representative Alkynes over Nic[a] in EtOH (15 mL)[b]

substrate (10 mmol)	initial rate[c]	t_{max},[g] min	semihydrogenated compd (%)[d]	Δ[e]	t_{100},[f] min
$C_6H_5C{\equiv}CH$	22	11.5	styrene (90%)	0.5	25
1-octyne	25	12	1-octene (80%)	0.4	30
2-hexyne	37	6.5	*cis*-2-hexene (96%)	3.7	60
3-hexyne	44	5.5	*cis*-3-hexene (98%)	4.6	60
1-phenyl-1-propyne	20	13	*cis*-1-phenyl-1-propene (90%)	~1.1	35

[a] From *t*-AmONa; ratio of Ni/reactant of 1/20 (in moles). [b] At 25 °C, 1 atm, and 2500 revolutions/min. [c] Average rate from 0 to 20% reaction, in cubic centimeters of H_2 at STP per minute. [d] Determined by GLC analysis with internal standards. [e] Δ represents the ratio of hydrogen uptake rates before and after the maximum percent of semihydrogenation products are obtained. [f] Time for uptake of 20 mmol of hydrogen, i.e., 100% of the theoretical amount. [g] Time for the maximum percent of semihydrogenated compound.

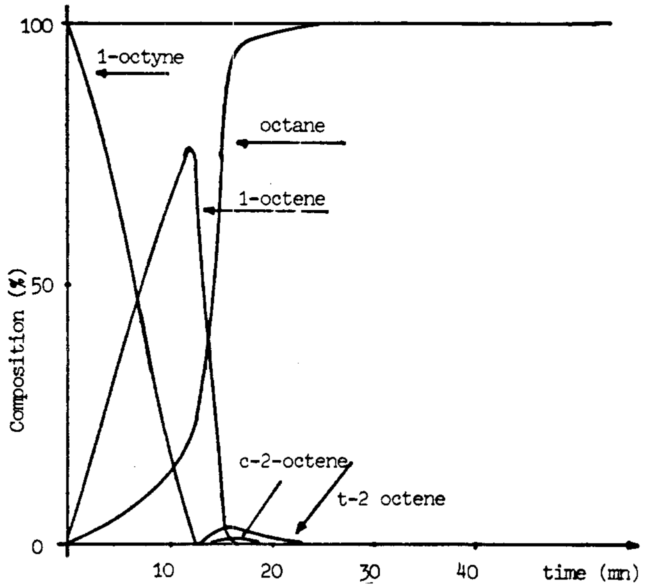

Figure 1. Progress of the hydrogenation of 1-octyne (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

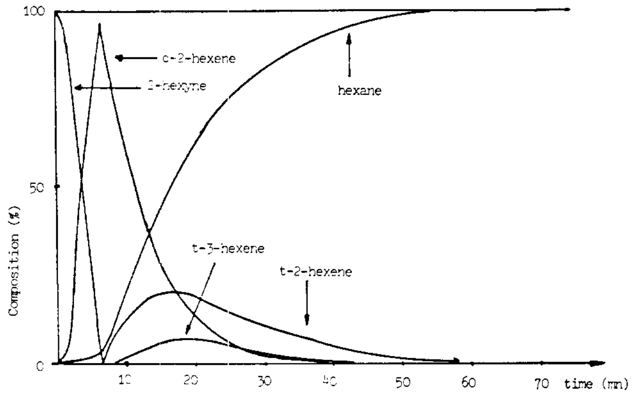

Figure 2. Progress of the hydrogenation of 2-hexyne (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

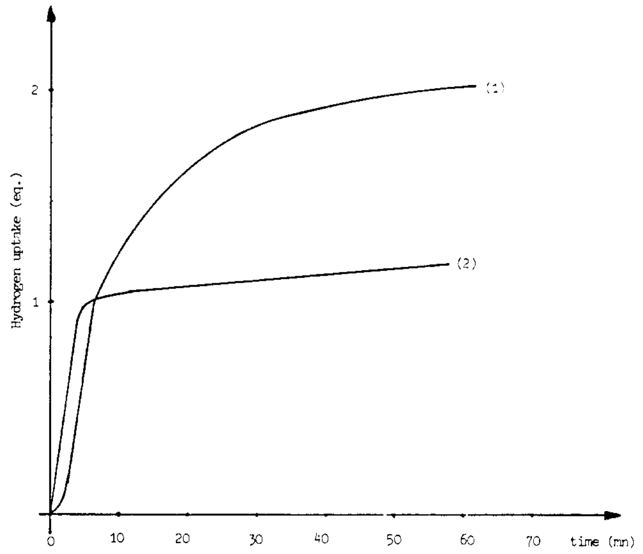

Figure 3. Hydrogenation curves of 2-hexyne (1) without added quinoline and (2) with added quinoline (quin/Ni ratio of 10).

minute aliquots syringed at various times.

Comparison of Figures 1 and 2 shows that alkane formation, although slow in both cases during the first half-reaction, begins earlier with 1-alkynes than with disubstituted ones. This is a well-known phenomenon for nickel catalysts, due to hydrogenation without desorption of the 1-alkene.[19]

It is also interesting to note that hydrogenation of alkene to alkane became faster only when 1-octyne had nearly disappeared and, overall, that isomerization of the alkene only began when all the alkyne had been consumed. It is well-known that, generally, side reactions may be minimized by poisoning the catalyst.[3] However, poisoning will be of practical interest only if it is easy to perform and, overall, is reproducible. Thus, in order to improve still more the practical selectivity of Nic, we tested the influence of quinoline added just before the substrate. Illustration of the observed results is given in Figure 3. It is clear that quinoline allows one to obtain more easily the maximum percentage of the semihydrogenated product. Moreover, GLC analysis showed a dramatic decrease of cis–trans isomerization (after $t_{50\%}$). It may be seen from the literature data[20] that Nic are among the best catalysts for semihydrogenation of disubstituted alkynes and that they compare very favorably for semihydrogenation of 1-alkynes. The next paper[14] will confirm this assertion.

Hydrogenation of Alkenes. Having demonstrated that Nic might be of interest for the semihydrogenation of alkynes, we decided to examine the hydrogenation of alkenes over Nic in order to determine the possible sensitivity of these catalysts to alkene structure.

For this study, the Nic prepared from *t*-AmONa as activating agent was selected. We first studied the influence of the hydrogenation solvent since it is well-known that this parameter is of great importance for alkene hydrogenation.[3] The main results are reported in Table VI. Here again, alcohols appeared to be the most efficient solvents.

However, comparison of data from Tables I and VI led us to an intriguing observation. Indeed, with some solvents, such as AcOEt, the reduction time of 1-octene to

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(19) See, for example: L. K. Freidlin and Y. Y. Kaup, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1660 (1962).

(20) E. N. Marwell and T. Li, *Synthesis*, 457 (1973).

Table VI. Influence of the Nature of Solvent on the Catalytic Hydrogenation of 1-Octene (10 mmol) over Nic[a, b]

solvent[c]	$t_{50\%}$,[d] min	solvent[c]	$t_{50\%}$,[d] min
H_2O	very slow	THF	95
MeOH	2.5	DME	14.5
EtOH (abs)	3.5	dioxane	25
EtOH (95%)	very slow	toluene	75
i-PrOH	5	benzene	105
$MeOCH_2CH_2OH$	4	cyclohexane	26
AcOEt	12	*n*-hexane	90
DMF	20		

[a] At 25 °C, 1 atm and 2500 revolutions per min. [b] From *t*-AmONa as activating alkoxide, ratio of Ni/1-octene of 1/20 (in moles) determined by atomic absorption after each run. [c] Volume 15 mL. [d] Time for uptake of 5 mmol of hydrogen, i.e., 50% of the theoretical amount.

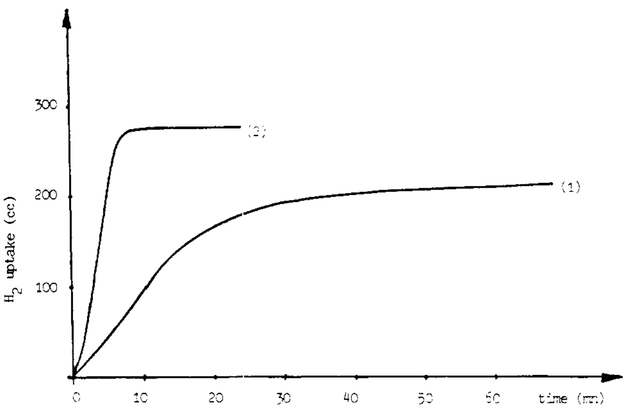

Figure 4. Hydrogenation curves of (1) 10 mmol of pure 1-octene and (2) a mixture of 1-octene (10 mmol) and 1-octyne (1 mmol) over Nic (0.5 mmol) in AcOEt (15 mL) at 25 °C (1 atm).

octane was the same or even longer than the reduction time of 1-octyne to octane! Among the hypotheses which might be anticipated, we retained the following: in these solvents (and possibly in some others), some new species, very active for 1-octene hydrogenation, were formed during the reduction of 1-octyne. Comparison of hydrogenation curves pictured in Figure 4 shows the validity of this hypothesis.

With the aim of knowing if this observation was general (and not specific to 1-octyne), 1-octene was hydrogenated in the presence of 10% phenylacetylene (Table VII). Comparison of Tables I and VII shows that the presence of phenylacetylene does not strongly change the reduction of 1-octene in solvents where this reduction is already fast. On the contrary, a dramatic acceleration was observed in other solvents. For the present time, we have no explanation for this observation which, however, may be of practical interest.

Hydrogenation Reproducibility. Alkene hydrogenations are often much more sensitive than alkyne hydrogenations to certain factors such as inadvertent poisoning, reagent and solvent quality variations, etc.[21] Thus, it was of interest to test the reproducibility of the hydrogenations and thus of the preparation of Nic (from *t*-AmONa). Hydrogenation of 10 mmol of 1-octene in EtOH (Ni/reactant ratio of 1/20) was selected. In ten hydrogenations, the time required for half-hydrogenation ($t_{50\%}$) was always between 3.25 and 3.75 min, thus demonstrating the reproducibility of all steps.

Table VII. Catalytic Hydrogenation of 1-Octene (10 mmol) over Nic[a] in the Presence of $C_6H_5C{\equiv}CH$ (1 mM)[b]

solvent[c]	$t_{50\%}$,[d] min	$t_{90\%}$,[d] min
H_2O	73	very slow
MeOH	2.5	7.5
EtOH (abs)	4	8
EtOH (95%)	9	20
i-PrOH	5.5	17
$MeOCH_2CH_2OH$	4	9
AcOEt	2.5	7
DMF	14	55
THF	9.5	48
DME	3	15
dioxane	4	16
toluene	7	25
benzene	12	39
cyclohexane	4.5	12
n-hexane	12	65

[a] At 25 °C, 1 atm, and 2500 revolutions/min. Ratio of Ni/1-octene of 1/20 (in moles) determined by atomic absorption after each run. [b] In all cases it was found that all the phenylacetylene was hydrogenated first. [c] Volume 15 mL. [d] Corrected for the hydrogenation time of 1 mmol of phenylacetylene.

Table VIII. Hydrogenation of Alkenes (10 mmol) over Nic[a] in EtOH[b]

alkene	initial rate[c]	$t_{50\%}$[d]	$t_{100\%}$[e]
1-pentene	23	5.5 min	27 min
1-hexene	35	3.5 min	25 min
1-octene	34	3.5 min	28 min
styrene	44	3 min	10 min
allylbenzene	32	4.5 min	13 min
cis-2-hexene	12	11 min	60 min
trans-2-hexene	12	11 min	60 min
α-methylstyrene	28.5	4.5 min	15 min
2-methyl-1-hexene	9.5	13 min	90 min
2-methyl-2-hexene	0.5	>8 h	
cyclopentene	23	5 min	14 min
cyclohexene	10	13 min	70 min
1-methylcyclohexene	0.15	>10 h	
cycloheptene	22	5.5 min	15 min
norbornene	33	4.5 min	12 min
cyclooctene	3	70 min	5.5 h
cyclododecene[f]	2.8	58 min	6 h

[a] At 25 °C, 1 atm, and 2500 revolutions/min. Nic from *t*-AmONa as activating agent, ratio of Ni/reactant of 1/20 (in moles). [b] Volume 15 mL. [c] Average rate from 0 to 20% reaction, in cubic centimeters of H_2 at STP per minute. [d] Time for uptake of 5 mmol of hydrogen, i.e., 50% of the theoretical amount. [e] Time for uptake of 10 mmol of hydrogen, i.e., 100% of the theoretical amount. [f] Cis/trans mixture, 35/65.

Furthermore, these results suggest a low sensitivity of Nic to common poisoning. (This property will be confirmed below.)

With the above data in hand, hydrogenation of a series of variously substituted alkenes was undertaken. All experiments were performed in EtOH with a Ni/reactant ratio of 1/20 at 2500 revolutions/min. The main characteristics of these hydrogenations are collected in Table VIII.

Comparison of hydrogenation curves obtained with monosubstituted alkenes (Figure 5) clearly shows that the chain length as well as the presence of a phenyl group does not dramatically change the progress of the hydrogenations; at the utmost, a slight acceleration was recorded when an aromatic ring was present on the chain (a similar observation was made by Brown and Ahuja with P_2 nickel[22]). However, it must be noted that the relative dif-

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(21) We thank one of the referees for his comments on this point.

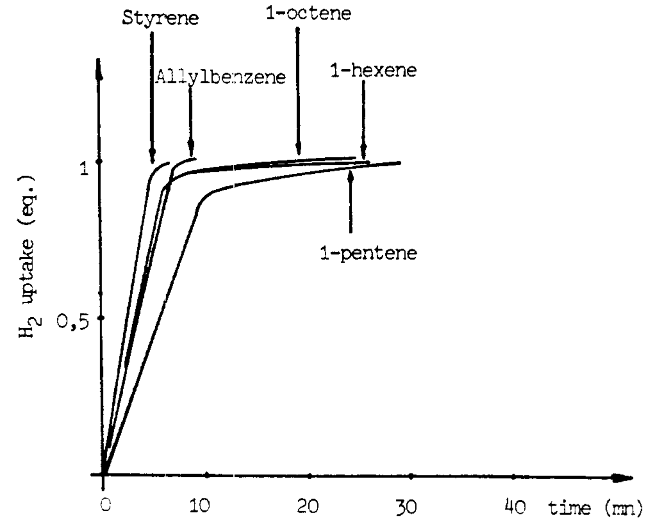

Figure 5. Hydrogenation of monosubstituted ethylenes (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

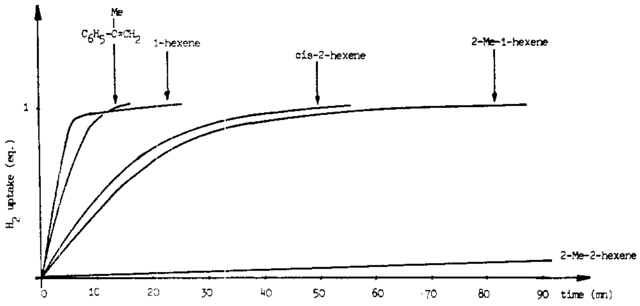

Figure 6. Hydrogenation of disubstituted ethylenes (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

ferences in reaction rates must be larger. Indeed, for the most rapid hydrogenations, the gas–liquid transfer does influence the observed reaction rate.

The reaction plots show various decreases in rate toward the end. This is a well-known phenomenon.[23] Indeed, during hydrogenation, some double bond isomerization occurs. It appears from Figure 5 that 1-pentene is only slightly isomerized during hydrogenation over Nic. Comparison of the hydrogenation curves of 1-pentene and 1-octene given by Brown[22,23] for P_1 and P_2 nickel shows that, even with the latter, nonnegligible isomerization may occur with 1-octene although this side reaction only reached 2 mol % at $t_{50\%}$ for 1-pentene hydrogenation. Thus, it was decided to measure the isomerization propensity of Nic for 1-octene. With 1-octene, 3% 2-octenes were found at $t_{50\%}$ and 6% (4% trans, 2% cis) at $t_{90\%}$. [Note that isomerization of 1-hexene reached 9% (7% trans, 2% cis) at $t_{90\%}$.] Thus, it may be concluded that alkene isomerization over Nic is not an important side reaction, even if slightly larger than over P_2 nickel.

On the other hand, Nic are very sensitive to double bond substitution as may be observed from Figure 6. (Note that in these cases, the gas–liquid transfer rate is scarcely important.) This property is very interesting for selective hydrogenations. Here again, the acceleration due to the presence of the aromatic ring was observed. The sensitivity to the structure of the alkene was also well documented with the hydrogenation of cycloalkenes (Figure 7, where the hydrogenation curve of *cis*-2-hexene was reported for comparison).

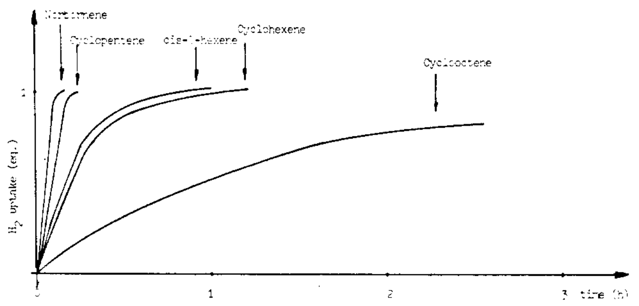

Figure 7. Hydrogenation of cycloalkenes (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

Table IX. Influence of Ni/Reactant Ratio for the Hydrogenation of 1-Octene over Nic[a] (0.2 mmol) in EtOH (15 mL)[b]

Ni/reactant ratio	initial rate[c]	$t_{100\%}$,[d] min
1/15	35	5
1/37.5	35	12
1/75	35	26

[a] From *t*-AmONa. [b] At 2500 revolutions/min. [c] Average rate from 0 to 20% reaction, in cubic centimeters of hydrogen at STP per minute. [d] Time for uptake of 1 equiv of hydrogen.

Double bond strain markedly promotes hydrogenation as is evidenced by norbornene hydrogenation. Other cycloalkenes were readily reduced with the following order of reactivity: $C_5 \approx C_7 > C_6 > C_8$. It is interesting to note that with P_1 and P_2 nickel,[22,23] the reactivity order was norbornene > $C_5 > C_8 > C_6$, showing an unexpected inertness of C_6. With Nic, cyclohexene is less reactive than cycloheptene but much more reactive than cyclooctene. This low reactivity of large rings seems to be the rule with Nic since a mixture of cyclodecenes (cis and trans) led to a hydrogenation curve similar to the one obtained for cyclooctene.

The influence of the Ni/reactant ratio was briefly studied for the hydrogenation of 1-octene. As may be seen from Table IX, low Ni/1-octene ratios may be used without a decrease in the rate.

Turnover and Stability on Storage. Another important property of a catalyst is conventionally appreciated by the number of turnovers. A number of turnovers of 1000, determined as described by Strohmeier,[24] was obtained in 6 h for the hydrogenation of 1-octene over Nic (from *t*-AmONa) in EtOH. After 6 h, the catalyst had lost less than half of its activity. However, this loss of activity is overestimated since each addition of 1-octene led to the formation of more alkane. So the solvent became richer in octane which is a bad hydrogenation solvent.

Moreover, the experiments performed to determine the number of turnovers (see Experimental Section) are very similar to the procedure used by Hussey et al. to evaluate the sensitivity of a catalyst to common poisoning.[25] Figure 8 describes the hydrogenation curves for the first four successive 15-mmol injections of 1-octene. It is clear that no noticeable variation in rate was recorded, at least for the first injections.

The above results strongly support the idea of the low sensitivity of Nic as regards common poisoning. This conclusion already appeared from the study of the stability on storage tested for the hydrogenation of alkynes (Table

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(22) C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, **38**, 2226 (1973).

(23) C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970), and references cited therein.

(24) W. Strohmeier and H. Steigerwald, *Z. Naturforsch., B*, 30(9), 816 (1975).

(25) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968).

Table X. Selective Catalytic Hydrogenations of Dienes or Olefines Mixtures over Nic[a] in EtOH[b,c]

compd(s) (each 10 mmol)	$t_{\max}$,[i] min	Δ[d]	product compsn[e] (%)	$t_{100\%}$[f]
1-octene, 2-methyl-1-hexene	9	4.2	octane (93), 2-octenes (7), 2-methyl-1-hexene (100)	2.5 h[g]
1-octene, cyclohexene	7	3.2	octane (93), 2-octenes (6), 1-octene (1), cyclohexene (100)	2.25 h
4-vinylcyclohexene	7.5	10	4-ethylcyclohexene (98)	3 h
2-methyl-1,5-hexadiene	7	3.4	2-methyl-1-hexene (98)	1.5 h[g]
1,3-cyclohexadiene	12	55	cyclohexene (98)	7.5 h
1,3-cyclooctadiene	10.5	60	cyclooctene (98)	>10 h
1,5-cyclooctadiene	14	15	cyclooctene (93)	4 h
2-methyl-1,3-butadiene	6.5	~1	2-methyl-1,3-butadiene (traces), 2-methyl-3-butene (15), 2-methyl-2-butene (45), 2-methyl-1-butene (35)	>4 h
norbornadiene	7.5	1	norbornene (85)[h]	13 min

[a] Prepared from NaH-*t*-AmONa-Ni(OAc)$_2$ (40/20/10). [b] Volume 15 mL. [c] At 25 °C, 1 atm, and 2500 revolutions/min. Ratio of Ni/reactant of 1/20 (in moles). [d] Δ represents the ratio of hydrogen-uptake rates before and after the maximum percent of semihydrogenation products are obtained. [e] At maximum percent of semihydrogenated product. Determined by GLC analysis with internal standards. [f] Time for uptake of 20 mmol of hydrogen. [g] In this case, complete hydrogenation was not achieved; indeed, 10% of the hardly reducible 2-methyl-2-hexene was formed by isomerization during the second part of the reaction. [h] The maximum percentage of norbornene was obtained after absorption of 1.15 equiv of hydrogen. [i] Time for maximum percent of semihydrogenated products.

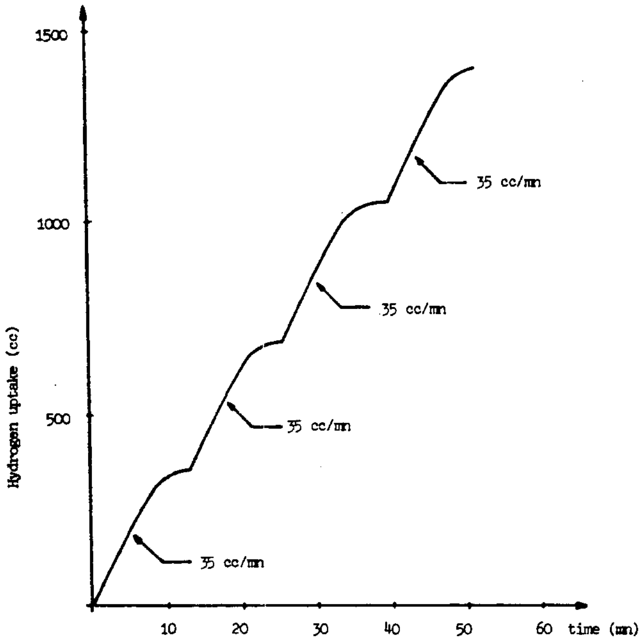

Figure 8. Plot of hydrogen absorption during the determination of the number of turnovers. Hydrogenation of 1-octene (four successive 15-mmol injections) over Nic (0.3 mmol) in EtOH (15 mL) at 25 °C (1 atm).

III). However, taking into account the large difference between the strongly adsorbed alkynes and the less adsorbed alkenes, stability on storage had to be tested for alkene hydrogenations.[26] In this aim, the nickel catalyst prepared from *t*-BuONa was selected as it had been found to be one of the most sensitive to storage. Indeed, it was found that this catalyst had lost 12% of its initial activity for alkyne hydrogenations after 7 months of storage (Table III). Under the same conditions (7 months of storage), this catalyst lost only 25% of its initial activity for cyclohexene hydrogenation. So it appears that the conclusions reached from alkyne hydrogenations also apply to alkene hydrogenations. Moreover, Nic may be considered as very slightly sensitive to common poisoning since simply distilled reagent-grade reactants were used and, above all, since solvents were purified by the more common procedures (see Experimental Section) and were not degassed.

Selective Hydrogenation of Alkene Mixtures and Dienes. The high sensitivity of hydrogenation catalysts to alkene structure generally indicates that they should be of interest in selective hydrogenations. Thus it was decided to examine the potential possibilities of Nic in this area. Results summarized in Table X illustrate the selectivity of Nic. The large Δ values are very favorable to selective hydrogenations. The only observed side reaction was a slight isomerization. However, examination of literature data indicates that Nic compare favorably with other nickel catalysts for their low isomerization propensity. Moreover, it is noteworthy that during 1,3-cyclohexadiene hydrogenation, no benzene formation was observed, a side reaction (disproportionation of the diene) which occurs even with highly specific nickel catalysts.[22]

A very intriguing observation was made for the hydrogenation of dienes. Indeed, comparison of hydrogenations of 1,3- and 1,5-cyclooctadienes (COD) showed that the cyclooctene hydrogenation time was dramatically longer when this hydrocarbon was formed from 1,3- than from 1,5-COD! One hypothesis to explain this observation may be the following: 1,3-COD is able to give some complex (possibly π allyl)[27] with active sites of Nic, leading to new sites active for diene reduction and poorly active for hydrogenation of isolated unsaturations.

To test this hypothesis, 1.5 mmol of 1,5-COD was first hydrogenated and then 10 mmol of cyclooctene was added when the absorption rate decreased to 1 cm^3/min. Under these conditions, total conversion to cyclooctane was achieved in 6 h. On the contrary, the same experiment, using 1,3- instead of 1,5-COD, needed more than 8 h for total conversion into cyclooctane. Furthermore, comparison of Tables VIII and X shows that the same feature is so for 1,3-cyclohexadiene. Thus the lowering of the hydrogenation rates by the presence of 1,3-dienes is not an artifact. This phenomenon will be studied as a possibility for modifying the catalyst properties.

It must be noted that isoprene was selectively hydrogenated to a mixture of three methylbutenes. Possible selective hydrogenation toward one of the possible methyl butenes is currently under investigation.

Hydrogenation of Carbonyl Compounds. It is well-known that under ambient conditions, carbonyl com-

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[26] We gratefully acknowledge one of the referees for his helpful suggestion on this point.

[27] D. M. Roundhill, *Adv. Organomet. Chem.*, 13, 273 (1975).

Table XI. Hydrogenation of Carbonyl Derivatives over Nic[a] in EtOH[b]

carbonyl compd (10 mmol)	$t_{50\%}$,[c] min	$t_{100\%}$,[d] h	product (% yield[e])
5-nonanone	130	9	5-nonanol (98-100)
acetophenone	37	2.5	1-phenylethanol (98-100)
cyclohexanone	56	2.75	cyclohexanol (98-100)
mesityl oxide	12[f]	4.5	4-methyl-2-pentanol (98-100)

[a] At 25 °C, 1 atm, and 2500 revolutions/min. Nic prepared from *t*-AmONa; ratio of Ni/reactant of 1/20 (in moles). [b] Volume 15 mL. [c] Time for uptake of 5 mmol of hydrogen. [d] Time for uptake of 10 mmol of hydrogen. [e] Determined by GLC analysis with internal standards. [f] At $t_{50\%}$ GLC analysis indicated the following product distribution: mesityl oxide, trace; methyl isobutyl ketone, 99-100%; 4-methyl-2-pentanol, traces. Then the observed absorption rate was slowed (Δ = 12).

pounds are generally hardly hydrogenated over nickel catalysts.[3] A few of them (W_7, W_6, and modified W_4[3] Raney nickels and Brown's P_2 nickel[22]) allow these reductions under rather mild conditions. However, these catalysts are not without disadvantages. Thus, W_7 and W_6 Raney nickels are of very poor stability on storage. Moreover, W_6 appears to be hazardous.[3] W_4 is more easily prepared than W_6 and W_7 and also is more stable on storage, but the modifications needed for carbonyl hydrogenations are not simply carried out.[28] On the contrary, Brown's P_2 nickel is easily prepared[22] but only slowly promotes hydrogenation of saturated carbonyl compounds.[29] Note that the very slow hydrogenation of carbonyl compounds may be a good property when selective hydrogenations of carbon-carbon double bonds are wanted with unsaturated carbonyl derivatives. However, the counterpart is a limitation of the catalyst for carbonyl group hydrogenations.

Taking into account the results obtained in this laboratory for the chemical reductions of carbonyl compounds with NiCRA,[11] a brief exploration of carbonyl hydrogenation over Nic was performed (Table XI and Figure 9). Of course, carbonyl groups were hydrogenated more slowly than averagely reactive double bonds. However, alcohols were obtained in very good yield in 2.5-9 h at 25 °C (1 atm).

The case of mesityl oxide deserves a special comment. Indeed, at $t_{50\%}$ (reached much more rapidly than with P_2 nickel[30]) the reaction mixture was constituted of fairly pure methyl isobutyl ketone (see footnote *f*, Table XI). In other words, Nic promote a rather easy hydrogenation of carbonyl groups, but the difference between the double bond and carbonyl hydrogenation rates is large enough to allow selective hydrogenation of carbon-carbon π bonds. In the next paper[14] we shall see some further illustrations of this important property.

Conclusion

Some complementary comments have to be made to conclude this work on the introduction of these new nickel catalysts.

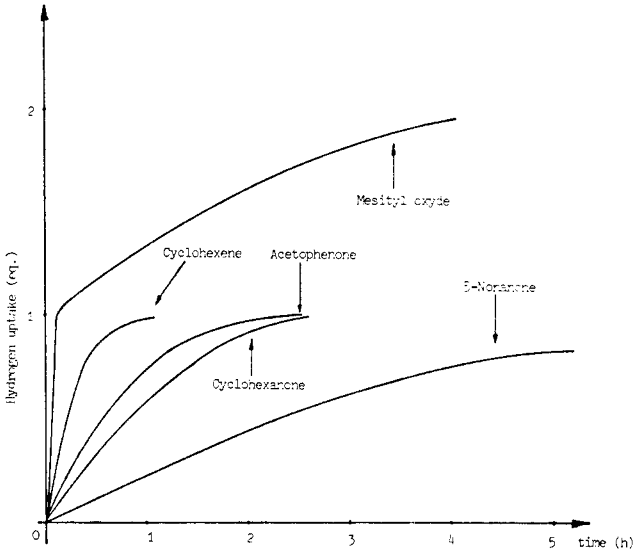

Figure 9. Hydrogenation of carbonyl compounds (10 mmol) over Nic (0.5 mmol) at 25 °C (1 atm).

When compared to the well-known Raney nickels,[3] Nic appear as more interesting from several points of view. Thus, they are easily and reproducibly prepared, are not pyrophoric, are stable on storage, are unhazardous, and allow selective reduction of double or triple bonds with a low isomerization propensity. Moreover, they allow hydrogenations of carbonyl derivatives under ambient conditions.

In fact, the properties of Nic more directly compare with those of Brown's P_1 and P_2 nickel,[31] although their compositions are completely different. Indeed, the P nickels contain a large quantity of nickel boride.[9,32] Of course, the actual structure of Nic is still unknown, but it may be thought, on the basis of the properties of complex reducing agents[10,11] and from the present study, that they are constituted of nickel hydrides as well as nickel alkoxides. Moreover, some sodium alkoxide and perhaps some indestructible sodium hydride may be associated within the unsoluble nickel framework.

Coming back to the comparison between P nickel borides and Nic, it can be seen that, to a certain degree, they are complementary. Indeed, for olefin hydrogenations, both are very sensitive to the double bond structure and show a rather low propensity toward isomerization. On the other hand their respective selectivity toward cycloalkenes is different, and unlike P_2 nickels,[22] Nic do not have a propensity toward disproportionation. With respect to acetylenic semihydrogenations, both are highly selective. However, P_2 nickel used with ethylenediamine[33] seems slightly better than Nic for semihydrogenation of disubstituted alkynes while Nic seems slightly better for monohydrogenations of 1-alkynes.

P_1 and P_2 nickels only slowly promote hydrogenation of carbonyl groups while Nic do so fairly rapidly. Thus Nic may be more easily used for carbonyl hydrogenations under mild conditions. Moreover, Nic also promote the selective hydrogenation of the carbon-carbon double bond in unsaturated ketones. Perhaps P_2 nickels should be more selective in special cases of unsaturated carbonyl compounds, owing to their very low ability to promote hy-

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(28) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946), and references cited therein.

(29) S. Mitsui, H. Saito, Y. Yamashita, M. Kaminaga, and Y. Senda, *Tetrahedron*, **29**, 1531 (1973); T. W. Russell, D. M Duncan, and S. C. Hansen, *J. Org. Chem.*, **42**, 551 (1977).

(30) T. W. Russell and R. C. Hoy, *J. Org. Chem.*, **36**, 2018 (1971).

(31) A direct comparison of the activity of Nic and P_2 nickel has already been described in ref 13.

(32) P. C. Maybury, R. W. Mitchell, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 534 (1974).

(33) C. A. Brown and V. K. Ahuja, *J. Chem. Soc., Chem. Commun.*, 553 (1973).

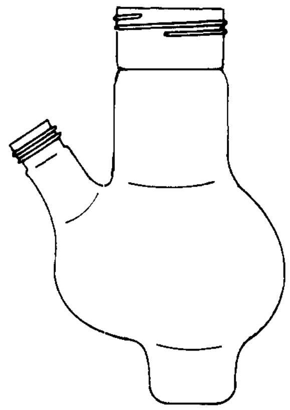

Figure 10. Hydrogenation vessel.

drogenation of carbonyl groups. However, as we shall see in the next paper,[14] Nic allow the resolution of some difficult cases of such selective hydrogenations.

Finally, as previously noted, the originality of Nic consists in their preparation from sodium hydride and alkoxides, allowing variations in their properties by varying the nature of the activating alkoxides. Moreover, it has been shown that complex reducing agents may be obtained from a large variety of metal salts, including transition-metal salts, as well as zinc or cadmium salts.[11] Thus it may be conjectured that a very large area of investigations is now opened in the field of hydrogenation catalysts.

Experimental Section

Materials. Fluka sodium hydride (50–60% in oil) was used and washed several times with THF in the reaction flask under nitrogen. Badische Anilin reagent-grade THF was distilled from benzophenone–sodium couple before use. (The absence of peroxides was tested for before each run.) Prolabo nickel acetate was dried under vacuum for 16–20 h at 100–110 °C and stored in a vacuum desiccator with P_2O_5 filling.

All activating alcohols were distilled from sodium. All chemicals were either commercial (Fluka or Aldrich) or prepared by classical procedures. They were purified by either distillation, recrystallization, or column chromatography before use. Reagent-grade solvents were used, after purification by classical procedures. DME, toluene, thiophene-free benzene, cyclohexane, and *n*-hexane were refluxed over sodium metal and then distilled and kept over sodium wires. *i*-PrOH and $MeO{-}CH_2CH_2OH$ were distilled from sodium metal while MeOH and EtOH were distilled from magnesium. Dioxane was purified as recommended by Milas.[34] DMF was dried several days over molecular sieves and then distilled under reduced pressure. Ethyl acetate was dried over potassium carbonate and then distilled over phosphorus pentoxide. In no case were these solvents degassed. Nitrogen R, argon U, and hydrogen (L'Air Liquide) were used.

General Methods. GLC analyses were performed on a Girdel 300, Girdel 3000, or Carlo-Erba GI 452 apparatus (flame ionization) equipped with squalene, Carbowax 20-M, and OV-101 capillary columns (50 m) or 5 m × $^1/_8$ in. columns packed with 15% UCON 50 HB 2000 on Chromosorb P (80–100 mesh).

IR spectra were recorded with a Perkin-Elmer 457 spectrometer and NMR spectra with Perkin-Elmer R 12 instrument. Nickel titrations were performed with a Varian Techtron atomic absorption photometer (Model 1200) used at 352.4 nm. X-ray data for the evaluation of the particle size were obtained from a Rigaku Miniflex diffractometer.

Preparation and Storage of Catalysts. The preparation of Nic is exemplified in the case of *t*-AmONa as activating alkoxide. Sodium hydride (60 mmol) was placed, under nitrogen, in a four-necked flask equipped with a cold condenser, a thermometer, a dropping funnel, and a mechanical stirrer. After being washed three times with anhydrous THF, sodium hydride was covered with 20 mL of THF. Nickel acetate (10 mmol) and THF (5 mL) were then successively added to the stirred suspension. After the mixture was heated to 45 °C, *t*-AmOH (20 mmol) in 5 mL of THF was added dropwise. A black coloration rapidly developed. After being stirred for 3 h at 45 °C, the reaction medium was allowed to cool to room temperature. The catalyst suspension was then syringed and stored under argon in a two-necked flask (equipped with two stopcooks) in which was placed a magnetic stirrer. For each run, after a short period of stirring, the catalyst (1.5 mL = 0.5 mmol of Ni) was syringed through one stopcook while argon was introduced through the other.

Hydrogenation Apparatus and General Procedure. All experiments were conducted with a classical apparatus for atmospheric-pressure catalytic hydrogenation equipped with the hydrogenation vessel pictured in Figure 10. Stirring was achieved by means of a star-shaped magnetic stirrer dragged by a U-shaped magnet held on the axis of a motor.

The general procedure is exemplified for the hydrogenation of 1-octene over Nic in EtOH. EtOH (10 mL) was placed in the hydrogenation vessel and all the apparatus purged several times with hydrogen. The catalyst (1.5 mL, i.e., 0.5 mmol of Ni) was then introduced. The neutralization of excess NaH was immediate. When aprotonic solvents were used, five drops of *t*-AmOH was added to ensure neutralization of excess NaH. After the hydrogen cylinder was filled and the water levels equalized, the stirring was adjusted to 2500 revolutions/min (monitored by a stroboscope). 1-Octene (10 mmol) in EtOH (5 mL) was then syringed into the hydrogenation vessel (the chronometer was started at this time). (When quinoline was used as a catalyst poison, it was introduced into the hydrogenation vessel just before the substrate.) The progress of hydrogenation was then followed in a classical manner, either by recording the hydrogen uptake vs. time or by sampling 0.1-mL aliquots for GLC analysis. At the end of each run, the catalyst was filtered and the catalyst loading determined by atomic absorption spectroscopy after classical treatment. In all cases, 1.5 mL of the catalyst suspension corresponded to 0.5 ± 0.03 mmol of nickel.

Determination of the Number of Turnovers. The number of turnovers was determined as follows. 1-Octene (15 mmol) was hydrogenated over Nic (0.3 mmol) in 15 mL of EtOH at 2500 revolutions/min. Whenever the hydrogen-uptake rate decreased to less than 1 cm^3/min, 15 mmol of 1-octene was again injected into the hydrogenation vessel. With this procedure, a number of turnovers of 1000 was reached in 6 h, i.e., 300 mmol of 1-octene was hydrogenated over 0.3 mmol of Nic, on the basis of hydrogen uptake.

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Registry No. 1-Octyne, 629-05-0; EtOH, 64-17-5; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0; *t*-AmOH, 75-85-4; $(Me)_3CCH_2OH$, 75-84-3; 2,5-dimethyl-2,5-hexanediol, 110-03-2; $Et(OCH_2CH_2)_2OH$, 111-90-0; C_6H_5OH, 108-95-2; NaH, 7646-69-7; *t*-AmONa, 14593-46-5; $Ni(OAc)_2$, 20998-57-6; *t*-BuONa, 865-48-5; *i*-PrONa, 683-60-3; $Et(OCH_2CH_2)_2ONa$, 52382-21-5; phenylacetylene, 536-74-3; 2-hexyne, 764-35-2; 3-hexyne, 928-49-4; 1-phenyl-1-propyne, 673-32-5; *cis*-2-hexene, 7688-21-3; *cis*-3-hexene, 7642-09-3; *cis*-1-phenyl-1-propene, 766-90-5; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 1-octene, 111-66-0; styrene, 100-42-5; allylbenzene, 300-57-2; *trans*-2-hexene, 4050-45-7; α-methylstyrene, 98-83-9; 2-methyl-1-hexene, 6094-02-6; 2-methyl-2-hexene, 2738-19-4; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; cycloheptene, 628-92-2; norbornene, 498-66-8; cyclooctene, 931-88-4; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5; 4-vinylcyclohexene, 100-40-3; 2-methyl-1,5-hexadiene, 4049-81-4; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; 2-methyl-1,3-butadiene, 78-79-5; norbornadiene, 121-46-0; 5-nonanone, 502-56-7; acetophenone, 98-86-2; cyclohexanone, 108-94-1; mesityl oxide, 141-79-7.

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