3082 *J. Org. Chem.* **1985**, *50*, 3082–3086

A New Route to an Active Form of Nickel. Transfer Hydrogenation of Alkenes and Carbonyl Compounds with 2-Propanol

Gian Paolo Boldrini, Diego Savoia, Emilio Tagliavini, Claudio Trombini,* and Achille Umani-Ronchi*

Istituto Chimico "G. Ciamician", Università di Bologna, 40126 Bologna, Italy

Received August 8, 1984

A new procedure for the transfer hydrogenation of alkenes and carbonyl compounds has been developed using an activated form of metallic nickel prepared by the thermal decomposition of nickel diisopropoxide in boiling 2-propanol. Monosubstituted alkenes undergo carbon–carbon double-bond migration more quickly than reduction; the 2-alkene produced is then reduced to alkane. Ketones are reduced in high yields, provided that acetone formed during the process is removed continuously. Unsaturated ketones are first converted to saturated ketones and then to alcohols, so by a careful control of the reaction course it is possible to stop the reaction at the first stage. Finally a comparison with the transfer hydrogenation of ketones, catalyzed by alkali metal isopropoxides in 2-propanol, has been performed.

A quickly accelerating interest has been devoted for almost a decade to the multidisciplinary area of highly dispersed metals for the unusual properties displayed in comparison to those of their bulk states.[1] General routes to metal powders consist of reductions of metal salts or oxides by means of hydrogen, hydrides, alkaline formaldehyde, or first or second group metals. Within this field we reported in recent years a quite general route to highly reactive forms of transition metals by the potassium–graphite reduction of metal halides in ethereal solvents.[2]

We now wish to describe the preparation of an active form of metallic nickel by the thermal decomposition of nickel diisopropoxide and its use as catalyst for the transfer hydrogenation of alkenes and carbonyl compounds in 2-propanol. Transfer hydrogenation reactions are known to be catalyzed by a variety of transition metals, typically the group 8–10[17] metals, under homogeneous or heterogeneous conditions.[3]

Results and Discussion

It is known that anhydrous nickel chloride reacts with 2 equiv of an alkali metal isopropoxide in absolute 2-propanol at 30 °C to afford the violet nickel diisopropoxide.[4] We have now found that in carrying out the reaction at higher temperature nickel diisopropoxide decomposes to metallic nickel,[5] hydrogen, and acetone. The overall process is described in Scheme I.[6] The rate of decomposition of nickel diisopropoxide depends on the temperature and the alkali metal cation. For example, starting from lithium or potassium isopropoxide, the overall process is virtually complete after 2 h at 60 °C and after 30 min at 100 °C, whereas when sodium isopropoxide is employed an 85% conversion is obtained after 2 h at 100 °C,[7] as determined by ^{1}H NMR spectroscopy, evaluating the amount of acetone produced and using benzene as internal standard.

Scheme I

$$2i\text{-PrOM} + NiCl_2 \rightarrow 2MCl + Ni(O\text{-}i\text{-}Pr)_2$$

$$Ni(O\text{-}i\text{-}Pr)_2 \rightarrow Ni + 2H + 2Me_2CO$$

$$M = Li, Na, K$$

Metallic nickel is at the beginning a black colloidal suspension which, on heating for several hours, undergoes a sintering process to form aggregates above the colloidal size, which precipitate out of the solution. Furthermore, after 7–8 h a considerable amount of nickel is attracted to the magnetic stirring bar, indicating that the mean particle size is larger than a ferromagnetic domain.[1]

A sample of powder, filtered under argon (*pyrophoric*), washed with 2-propanol, and dried under vacuum, was subjected to X-ray diffraction analysis (Debye–Scherrer camera, Cu Kα) and unambiguously identified as metallic nickel. Concerning the hydrogen produced, we have not yet obtained information about its fate; we believe that in part it becomes chemisorbed by the nickel clusters' surface.[8]

Colloidal nickel prepared by the preceding method effectively catalyzes the transfer hydrogenation of alkenes and ketones in boiling 2-propanol. The reactions are simply carried out by adding the organic substrate to a freshly prepared suspension of nickel in 2-isopropanol and stirring the mixture at 95–100 °C (external oil bath). In general the catalyst is prepared from lithium or potassium iso-

---

[1] Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153.

[2] (a) Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540. (b) *Ibid.* 541. (c) Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1981**, *46*, 5340. (d) *Ibid.* 5344. (e) *Ibid.* **1982**, *47*, 876. (f) Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *Ibid.* **1983**, *48*, 4108. (g) *J. Organomet. Chem.* **1984**, *268*, 97. (h) *Ibid.*, **1985**, *280*, 307.

[3] (a) Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567. (b) James, B. R. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 51.

[4] Baranwal, B. P.; Mehrotra, R. C. *Aust. J. Chem.* **1980**, *33*, 37.

[5] The thermal decomposition of $Li_2[Ni(i\text{-}PrO)_4]\text{-}LiBr\text{-}3THF$ to metallic nickel and acetone was previously reported: Kalies, W.; Witt, B.; Gaube, W. *Z. Chem.* **1980**, *20*, 310. Related preparations of metallic nickel involve the thermal decomposition of nickel di-*tert*-butoxide [(a) Schott, H.; Wilke, G. *Angew. Chem. Int. Ed. Engl.* **1969**, *11*, 877], nickel formate [(b) Krivanek, M.; Danes, V.; Nikolajenkov, V. *Collect. Czech. Chem. Commun.* **1964**, *31*, 1950], and nickel oxalate [(c) Hata, K.; Watanabe, K.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 775].

[6] The overall process of Scheme I does not take place with moderately wet 2-propanol (2% v/v of water) or replacement of anhydrous $NiCl_2$ with $NiCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}(PPh_3)_2$, or $NiCl_2$–1,2-dimethoxyethane.

[7] We were not able to establish the possible effect of coprecipitated alkali metal chloride on the decomposition of $Ni(O\text{-}i\text{-}Pr)_2$ by preparing it at 30–40 °C and filtering off MX. In fact the preparation of $Ni(O\text{-}i\text{-}Pr)_2$ cannot be driven to completion at this temperature, owing to the extremely low solubility of anhydrous $NiCl_2$ in 2-propanol.[4] Moreover the poor solubility of NaCl (0.75 g/L at 30 °C) and KCl (1.26 g/L at 30 °C) in 2-propanol requires washings of the reaction mixture with large amounts of solvent. We found that samples of 2-propanol containing 0.05% v/v of water cause the hydrolysis of $Ni(O\text{-}i\text{-}Pr)_2$, evidenced by the formation of a green precipitate.

[8] The ability of transition-metal surfaces to chemisorb hydrogen finds important applications in heterogeneous catalysis (MacKay, K. M. "Hydrogen Compounds of the Metallic Elements"; E. and F. N. Spon Ltd.: London, 1966) and in hydrogen storage and transport (Reilly, J. J.; Sandrock, G. D. *Sci. Am.* **1980**, *242*, 98). Concerning nickel catalysts, the dissociative chemisorption of hydrogen is exploited for determining their surface area, and it is assumed that each nickel atom of the surface links to a hydrogen atom: Lohrengel, G.; Baerns, M. *Appl. Catal.* **1981**, *1*, 3.

0022-3263/85/1950-3082$01.50/0

Table I. Transfer Hydrogenation of Alkenes[a]

entry	alkene (mol/L)	mol % Ni	time, h	% convn[b]	% alkane[b]	bp, °C	% double-bond migration[b]
1	1-decene (2.5)	2.5	40	82	62	174	15
2	1-decene (2.5)	5	7	89	60		26
3	1-decene (2.5)	10	7	93	88		3
4	1-undecene (0.83)	30	1.5	100	93	193	
5	(*E*)-2-octene (1.25)	20	2	100	96	124	
6	cyclooctene (2.5)	10	7	79	75	148	
7	2-methyl-1-heptene (2.5)	10	6	95	80	117	12
8	1,8-menthadiene (0.83)	30	1	100	85[c]	166	not determined
9	allyl benzyl ether[d] (2.5)	10	4	100	55	202	6

[a] The reactions are carried out on 5 mmol of catalyst at 95–100 °C (external bath). The products are identified by GC–mass spectrometry or by GC comparison with authentic samples. [b] Values estimated by GC. [c] The product is 4-isopropyl-1-methyl-1-cyclohexene: ^{1}H NMR (CCl_4, δ values from Me_4Si) 5.4 (m, 1 H, vinylic), 1.65 (pseudo s, 3 H), 0.95 (d, 6 H); parent ion in the mass spectrum at *m/e* 138 and base peak at *m/e* 95 (loss of the isopropyl radical). [d] The substrate undergoes partial hydrogenolysis.

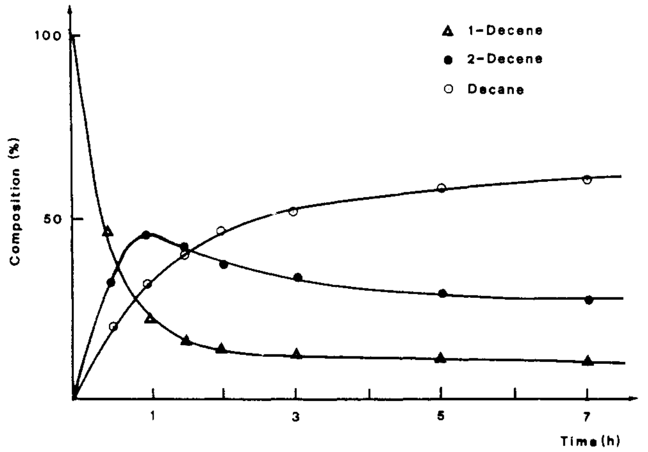


Figure 1. Time course of the reduction of 1-decene with 5 mol % of nickel in 2-propanol at 95 °C (Table I, entry 2). [1-Decene] = 2.5 M.

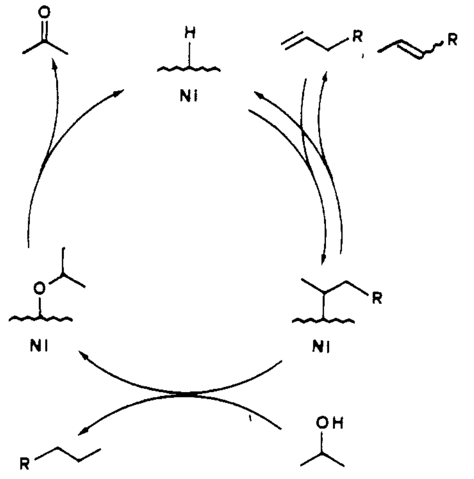
propoxide and nickel chloride in boiling 2-propanol, and the substrate is added 30 min after the appearance of black colloidal nickel. *Since the catalyst is quickly oxidized by air, its preparation and the subsequent reactions have to be carried out under an inert atmosphere.*

Transfer Hydrogenation of Alkenes. Mono- and disubstituted carbon–carbon double bonds are effectively reduced as shown in Table I in refluxing 2-propanol. The maximum reduction rate is observed in the early phase, and then it slows down probably as a consequence of sintering, which reduces the overall surface area of the catalyst.

In the case of monosubstituted alkenes the reduction reaction is accompanied by carbon–carbon double-bond migration, which is the faster process in the early phase. Figure 1 shows the typical conversion–time profile for the reduction of 1-decene. The highest amount of double-bond migration with 2.5, 5, and 10 mol % catalyst was observed after 7, 1, and 0.5 h, respectively.

The main isomeric alkene produced is 2-decene (*E*/*Z* = 6/4 by GC analysis) as shown by the ^{1}H NMR spectrum of the crude product mixture. The experimental results fit with the catalytic cycle sketched in Scheme II. A reversible hydrometalation of the alkene leads to an alkyl–nickel intermediate,[9] which, accounting also for double-bond migration, gives, upon protonation by 2-propanol, the alkane and a nickel isopropoxide species. The latter undergoes a β-hydrogen transfer to the metal, forming acetone and restoring the catalyst.[10] Attempts to drive the reaction toward a clean 1- to 2-alkene isomerization were made by replacing 2-propanol with aprotic solvents. The catalyst for this purpose was prepared in the usual way in a flask equipped with a sintered frit in a side arm, which allows the filtration of 2-propanol under a positive argon pressure. The best results (75–85% 2-decene) were obtained by adding to the catalyst (30 mol %) 1-decene (30 mmol) dissolved in tetrahydrofuran or 1,4-dioxane (30 mL) and stirring the reaction mixture at the reflux temperature for 3 h; minor amounts of decane (10–15%) were always obtained.

Scheme II



Transfer Hydrogenation of Carbonyl Compounds. Several experiments have been carried out to establish the usefulness of this colloidal nickel as a catalyst for the transfer hydrogenation of ketones in 2-propanol according to eq 1. In the literature there are only few reports about

$$R_2C{=}O + Me_2CHOH \xrightarrow{Ni} R_2CHOH + Me_2C{=}O \quad (1)$$

transfer hydrogenations of ketones in alcohols in the presence of nickel catalysts.[11] To this purpose Raney

---

(9) The addition of Ni–H species to propene is known to be reversible and quite regioselective, giving propyl- and isopropylnickel intermediate in a 1/4 ratio: Bogdanović, B. *Adv. Organomet. Chem.* **1979**, *17*, 105. (π-Allyl)nickel complexes, which are probable intermediates, are omitted in Scheme II for brevity.

(10) Concerning metal–hydrogen-bond formation reactions via alkoxides, see: Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(11) (a) Kleiderer, E. C.; Kornfeld, E. C. *J. Org. Chem.* **1948**, *13*, 455. (b) Newham, J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1179. Many reports in the literature describe preparations of heterogeneous nickel catalysts (see, for example, ref 1, 2c,d, and 11c–g), but to our knowledge they have been applied to reductions other than transfer hydrogenation reactions. For leading references, see: (c) Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226. (d) Ashby, E. C.; Lin, J. J. *Ibid.* **1978**, *43*, 2567. (e) Caubère, P. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 599. (f) Klabunde, K. J.; Tanaka, Y. *J. Mol. Catal.* **1983**, *21*, 57. (g) Inba, S.; Rieke, R. D. *Synthesis* **1984**, 844.

Table II. Transfer Hydrogenation of Cyclohexanone[a]

entry	alkali metal	mol % Ni	t, h	T,[b] °C	% convn[c]
1	Li	10	0.5	95	≥95
2	Na	10	0.5	95	40
			1		80
			2		95
3	K	10	0.5	95	≥95
4	K	10	0.5	50[d]	45
			1		65
			3		93
5	K	5	2	95	75
			5		95

[a] The reactions are carried out on 0.1 mol of cyclohexanone (∼1.5 M) with continuous distillation of acetone. [b] External oil bath temperature. [c] Values estimated by GC analysis. [d] [Cyclohexanone] = 1 M.

nickel[11a] was used in large excess in refluxing alcohols for 16–24 h. Furthermore hydrogen transfer from 2-propanol to 2-butanone was reported to be catalyzed by nickel on silica[11b] preactivated at 450 °C for 8 h in flowing hydrogen.

We preliminarily chose cyclohexanone as a model substrate to verify the effect of the alkali metal, catalyst amount, and temperature on the reaction rate (Table II). The best results were achieved by starting from lithium or potassium isopropoxide and heating the reaction mixture at 95 °C (external oil bath). Under these conditions acetone can be continuously distilled off, so that the reaction is driven to completion. The reduced activity observed in entry 2 reflects the less efficient formation of colloidal nickel when sodium isopropoxide is used.[7] The reaction can be also effected at 50 °C (entry 4) in almost quantitative yield in 3 h; since under these conditions acetone cannot be removed, a lower concentration of cyclohexanone is used. Finally, reducing to half the catalyst amount (entry 5), a 10-fold reaction time is necessary to reach a 95% conversion.

In Table III the results obtained from working with simple saturated and aromatic ketones are collected. The reduction of 2- and 3-alkanones and cycloalkanones proceeds in good to excellent yields in 3–5 h using 10 mol % catalyst at 95–100 °C and distilling off acetone. Generally 0.1 mol of ketone was used, but the reaction scale can be easily raised to 1 mol (entry 3) without any problem. This makes this procedure particularly valuable for medium scale reductions.

Low diastereoselection is observed in the reduction of 1,4-cyclohexanedione (entry 7) and camphor (entry 9),[12] while 2-methylcyclohexanone (entry 8) gives a 1/1 mixture of cis and trans alcohols.[13] In the last case a direct comparison is possible with the transfer hydrogenation reaction catalyzed by ruthenium, osmium, and iridium[14] in 2-propanol. These catalysts, prepared by the sodium formate reduction of aqueous solutions of potassium hexachlororuthenate, -osmate, or -iridite, require longer reaction times (20–70 h) and greater amounts of catalyst (18–30 mol %) to give 30–60% yields of 2-methylcyclohexanol, slightly enriched in the cis isomer (60%).

Table III. Transfer Hydrogenation of Ketones[a]

entry	ketone	t, h	% alcohol[b]	bp or mp, °C
1	2-octanone	3	92	85 (18 torr)
2	2-undecanone[c,d]	7	78	126 (17 torr)
3	4-methyl-2-pentanone[d,e]	5	87	131
4	acetophenone	3	91	104 (20 torr)
5	3-pentanone	3	84	115
6	3-heptanone[d]	4	77	154
7	1,4-cyclohexanedione[f]	1	88[g]	96–99 (CHCl$_3$)
8	2-methylcyclohexanone	2	96[h]	61 (18 torr)
9	(+)-camphor[f]	5	75[i]	202–205 (hexane)

[a] Unless otherwise stated, the reactions are carried out on 0.1 mol of ketone (∼1.8 M) using 10 mol % of nickel prepared from NiCl$_2$ and LiO-*i*-Pr at 95–100 °C (external bath). [b] Values determined by GC analysis. [c] 5 Mol % of catalyst is employed. [d] The catalyst is prepared from NiCl$_2$ and KO-*i*-Pr. [e] The reaction is carried out on 1 mol of ketone in 400 mL of 2-propanol using 0.1 mol of catalyst. [f] 30 Mol % of catalyst are used. [g] GC analysis reveals the presence of 5% of 4-hydroxycyclohexanone. The diol is purified by silica gel column chromatography (hexane–ether 8/2); the ^{13}C NMR spectrum (acetone-d_6, δ values from Me$_4$Si) shows signals at 69.0 and 66.9 (C1 and C4 for trans and cis diol, respectively) in the 4/5 relative ratio and at 33.3 and 30.6 (C2, C3, C5 and C6 for trans and cis diol, respectively) in the 4/5 relative ratio too. Cf.: Cyr, N.; Perlin, A. S.; Whitehead, M. A. *Can. J. Chem.* **1972**, *50*, 814. [h] 2-Methylcyclohexanol is a 1/1 mixture of cis and trans diastereomers on the basis of the integral ratio of the ^{13}C NMR signals (CDCl$_3$, Me$_4$Si) of trans methyl (δ 18.3) and cis methyl (δ 16.3) carbons. Cf.: Pehk, T.; Kooskora, H.; Lippmaa, E. *Org. Magn. Reson.* **1976**, *8*, 5. [i] A mixture of *exo*- and *endo*-borneols in 1.4/1 ratio is obtained as determined by GC analysis. As a comparison, a 4/1 mixture of *exo*- and *endo*-borneols was prepared by NaBH$_4$ reduction of camphor (see ref 10).

Going from saturated to unsaturated ketones (Table IV) we could directly observe the competitive reduction of carbon–carbon vs. carbon–oxygen double bonds. 5-Hexen-2-one, cyclohexenone, and *β*-ionone first undergo a fast reduction of the carbon–carbon bond. Only when most of the starting ketone is consumed does the carbonyl reduction take place; therefore, a careful control of the reaction progression allows one to stop the reaction at the saturated ketone stage. Only in the case of 5-hexen-2-one was a significant amount of unsaturated alcohol (7%) observed after 0.5 h (entry 1).

When we tried to apply this methodology to aldehydes, we found that, in contrast with ketones, the reduction in boiling 2-propanol takes place stoichiometrically in nickel: for example, decanal affords decanol in 90%, 55%, and 18% yields with 50, 30, and 10 mol % catalyst, respectively. Self-condensation products (10–20%) are also observed. Analogously, benzaldehyde treated with 25 mol % nickel gives no more than 40% benzyl alcohol in 5 h together with about 5% higher boiling products.

Last we performed some experiments in order to estimate the possible contribution of minute amounts of alkali metal isopropoxides, which could be present in the reaction mixture, to the reduction course. A series of ketones were treated under Verley conditions[15] with an alkali metal isopropoxide in boiling 2-propanol (Table V). While 10 mol % nickel catalyst gives, for example, 95% cyclohexanol in 0.5 h (Table II, entry 1), 10 mol % lithium isopropoxide, under the same experimental conditions, requires 8 h to give 75% of the same alcohol (Table V, entry 4). Moreover self-condensation products in 10–20% yields are formed by alkali metal isopropoxide, while in the nickel-catalyzed reduction they are generally limited to less than 5% and sometimes virtually absent. The mechanisms operating in the Verley-type and Ni-catalyzed reductions are dif-

---

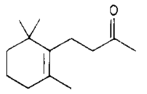
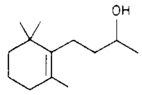
(12) The diastereoselective reduction of camphor to *exo*-borneol is in general achieved with aluminum hydrides: Brown, H. C.; Deck, H. R. *J. Am. Chem. Soc.* **1965**, *87*, 5620.

(13) 2-Methylcyclohexanone is diastereoselectively reduced to the trans or cis alcohol by means of alkoxyborohydrides and alkylborohydrides, respectively: Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

(14) Henbest, H. B.; Zurqiyah, A. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 604.

(15) Verley, M. *Bull. Soc. Chim. Fr.* **1925**, *37*, 871.

Table IV. Transfer Hydrogenation of Unsaturated Ketones[a]

entry	substrate	*t*, h	% convn[b]	products (%)[b]
1	5-hexen-2-one	0.5	85	2-hexanone (61), 2-hexanol (14), 5-hexen-2-ol (7)
		1.5	91	2-hexanone (15), 2-hexanol (75), 5-hexen-2-ol (tr)[f]
		4	95	2-hexanone (12), 2-hexanol (81), 5-hexen-2-ol (tr)
2	2-cyclohexen-1-one	1	50	cyclohexanone (47), cyclohexanol (tr)
		3	90	cyclohexanone (80), cyclohexanol (8)
		6	100[c]	cyclohexanone (14), cyclohexanol (75)
3	*β*-ionone	1	50	 (47)[d]  (tr)
		2	77	3,4-dihydro-*β*-ionone (75), 3,4-dihydro-*β*-ionol (tr)
		6	98	3,4-dihydro-*β*-ionone (8), 3,4-dihydro-*β*-ionol (86)[e]

[a] The reactions are carried out on 0.1 mol of substrate (~1.8 M) using 10 mol % of nickel prepared from $NiCl_2$ and LiO-*i*-Pr, at 95–100 °C (external bath). [b] Values determined by GC analysis. [c] Self-condensation products are detected in about 10% yield. [d] IR (neat) 1720 cm^{-1}; ^1H NMR (CCl_4, δ values from Me_4Si) 2.3 (m, 2 H), 2.05 (s, 3 H), 1.55 (s, 3 H), 1.3–2.1 (8 H), 1.0 (s 6 H); mass spectrum, *m/e* 194 (M^+); bp 126 °C (18 torr). [e] IR (neat) 3350 cm^{-1}; ^1H NMR (CCl_4, δ values from Me_4Si) 3.75 (m, 1 H), 2.4 (s, 1 H, OH), 1.65–2.25 (4 H), 1.6 (s, 3 H), 1.2–1.7 (6 H), 1.15 (d, 3 H), 1.0 (s, 6 H); mass spectrum, *m/e* 196 (M^+); bp 140 °C (18 torr). [f] Trace amount = tr.

Table V. Ketone Reductions Catalyzed by Alkali Metal Isopropoxides[a]

entry	ketone	metal, (mol %)	*t*, h	% convn[b]	% alcohol[b]
1	2-octanone	Li (25)	9	78	72
2	2-octanone	Na (25)	8	88	75
3	2-octanone	K (25)	9	43	30
4	cyclohexanone	Li (10)	8	85	75
5	2-methylcyclohexanone	Li (25)	8	80	67[c]
6	3-heptanone		8	67	60
7	5-hexen-2-one	Li (25)	8	75	62[d]

[a] The reactions are carried out on 50 mmol of ketone; the substrate is added to a solution of the alkali metal isopropoxide in absolute 2-propanol and stirred at 95–100 °C (external bath) with continuous distillation of acetone. The initial substrate concentration is ~1.8 M. [b] Values determined by GC analysis using C_8–C_{12} alkanes as internal standard. [c] The trans/cis ratio of diastereomeric 2-methylcyclohexanols is 4/1. See footnote *h* in Table III. [d] The product is 5-hexen-2-ol.

ferent as shown by the different diastereo- and chemoselectivities obtained in the reductions of 2-methylcyclohexanone (entry 8 in Table III and entry 5 in Table V), and of 5-hexen-2-one (entry 1 in Table IV, and entry 7 in Table V). Indeed lithium isopropoxide displays a good diastereoselectivity in the first case and an absolute preference to reduce the carbonyl group in the presence of isolated carbon–carbon double bond. These results make us believe that the presence of residual alkali metal isopropoxides in our catalytic system is negligible.

In conclusion, we have developed an alternative route to a very active nickel that can be of general utility for the reduction of alkenes and ketones. Provided that the most important precaution requires the use of an inert atmosphere since a short contact with air deactivates the catalyst, the simplicity of the procedure described makes it competitive with the use of standard hydrogenation techniques and of hydride transfer reagents in medium to large scale reductions.

Experimental Section

Materials and Analyses. All substrates were purchased from Fluka and used as received. Allyl benzyl ether was prepared in 88% yield under phase-transfer conditions (TEBA, 50% aqueous NaOH, allyl alcohol, benzyl chloride). 2-Propanol was obtained from Carlo Erba (RPE ACS, 99.5% pure). Anhydrous nickel chloride, available from Merck, was stored under argon in a Schlenk-type tube. Samples of nickel chloride made anhydrous by the $SOCl_2$ method[16] were also successfully used. The reactions were followed by gas chromatography (GC) using a Perkin-Elmer Sigma 3 instrument equipped with a $^1/_4$ in. × 6 ft column packed with 5% FFAP on silanized Chromosorb G, 80–100 mesh, with a nitrogen flow of 40 mL/min. Quantitative analyses were performed by means of a Perkin-Elmer Sigma 10 data station. All products were identified by comparison of their GC retention times and infrared, nuclear magnetic resonance, and mass spectra to those of samples commercially available or obtained by independent synthesis.

Transfer Hydrogenation of 1-Undecane (Table I, Entry 4). Typical Procedure for the Reduction of Alkenes. A 0.5 M solution of lithium isopropoxide is prepared by adding lithium (0.07 g, 10 mmol) to 2-propanol (20 mL) in a 150-mL two-necked flask equipped with a reflux condenser and connected to an argon line. Anhydrous nickel chloride (0.65 g, 5 mmol) is then added, and the reaction mixture is vigorously stirred with a magnetic stirring bar at 95–100 °C (external oil bath). Thirty minutes after the formation of black colloidal nickel, 1-undecene (2.58 g, 16.7 mmol) is introduced, and the reaction mixture is stirred at 95–100 °C. After 1.5 h 1-undecene is completely reacted as shown by GC. After cooling to room temperature, the reaction mixture is treated with water (2 mL) and filtered through Celite. The yield of undecane (93%) is determined by GC using dodecane as internal standard. **Undecane:** IR (neat, absorptions in cm^{-1}) 2950, 2870, 1470, 1380, 720; ^1H NMR (60 MHz, $CDCl_3$, δ values from internal Me_4Si) 1.25 (pseudo s, 18 H), 0.9 (t, 6 H); MS (70 eV, *m/e*, relative intensity) 156, (M^+, 10), 85 (25), 71 (45), 57 (100), 43 (85).

Transfer Hydrogenation of 2-Octanone (Table IV, Entry 1). Typical Procedure for the Reduction of Ketones (Tables II–IV). A 250-mL two-necked flask is equipped with a water-jacketed column connected to a distillation head and a Liebig condenser and joined to a double-manifold vacuum line which allows the apparatus to be evacuated and filled with argon. In such an apparatus the solvent can be refluxed or distilled simply by turning on or off the water cooling of the vertical column. A 0.5 M solution of lithium isopropoxide is prepared by adding the alkali metal (0.14 g, 20 mmol) to the reaction flask containing absolute 2-propanol (40 mL). Anhydrous nickel chloride (1.30 g, 10 mmol) is then added. The flask is sealed by placing a serum cap over one neck and plunged into an oil bath thermostated at 95–100 °C; the reaction mixture is stirred at this temperature with a magnetic stirring bar. Thirty minutes after the formation of black colloidal nickel, a solution of 2-octanone (12.8 g, 100 mmol) and undecane (internal standard) in 2-propanol (25 mL) is introduced by syringe through the serum cap. The reaction mixture is stirred at 95–100 °C with continuous removal of acetone by distillation, and the reaction course is followed by GC. After 3

---

(16) Pray, A. R. *Inorg. Synth.* **1957**, *5*, 153.

(17) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

h a 92% yield of 2-octanol is determined by GC. The flask is cooled to room temperature, and the reaction mixture is treated with water (4 mL) and filtered through Celite. The solvent is removed under reduced pressure and the product purified by silica gel column chromatography and distillation [10.5 g, 81% isolated yield, bp 85 °C (18 torr)]. **2-Octanol**: IR (neat, absorptions in cm^{-1}) 3400 (br); ^{1}H NMR (60 MHz, $CDCl_3$, δ values from internal Me_4Si) 3.8 (m, 1 H), 1.9 (s, 1 H, OH), 1.35 (m, 10 H), 1.2 (t, 3 H), 0.9 (t, 3 H); MS (70 eV, *m/e*, relative intensity) 130 (M^+, traces), 57 (7), 55 (16), 43 (20), 45 (100).

Acknowledgment. This work was supported by the Italian C.N.R. (Progetto Finalizzato Chimica Fine e Secondaria).

Registry No. 1-Decene, 872-05-9; 1-undecene, 821-95-4; (*E*)-2-octene, 13389-42-9; cyclooctene, 931-88-4; 2-methyl-1-heptene, 15870-10-7; 1,8-menthadiene, 138-86-3; allyl benzyl ether, 14593-43-2; cyclohexanone, 108-94-1; 2-octanone, 111-13-7; 2-undecanone, 112-12-9; 4-methyl-2-pentanone, 108-10-1; acetophenone, 98-86-2; 3-pentanone, 96-22-0; 3-heptanone, 106-35-4; 1,4-cyclohexanedione, 637-88-7; 2-methylcyclohexanone, 583-60-8; (+)-camphor, 464-49-3; 5-hexen-2-one, 109-49-9; 2-cyclohexen-1-one, 930-68-7; β-ionone, 79-77-6; 2-propanol, 67-63-0; Ni, 7440-02-0; lithium isopropoxide, 2388-10-5; sodium isopropoxide, 683-60-3; potassium isopropoxide, 6831-82-9.

2,4-Cyclohexadien-1-ones in Organic Synthesis. Intramolecular Diels–Alder Reactivity and the Oxa-di-π-methane Photorearrangement of Diels–Alder Adducts

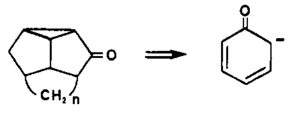
Arthur G. Schultz,* Frank P. Lavieri, and Thomas E. Snead

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received October 11, 1984

The preparation and intramolecular Diels–Alder reactions of a series of 6-alkenyl-6-(methoxycarbonyl)-2,4-cyclohexadien-1-ones are described. The resulting tricyclic β,γ-enones undergo the oxa-di-π-methane rearrangement to give substrates of potential use in the construction of polyquinane natural products. This methodology provides a means for construction of tetracyclic rings of type A by C-alkylation of the synthetic equivalence of enolate B.

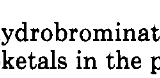
We have reported a general method for the construction of 6-alkyl-6-carbalkoxy-2,4-cyclohexadien-1-ones by Birch reduction–alkylation of *o*-hydroxybenzoic acid derivatives.[1] The chiral auxiliary technique has been used to prepare optically active 2,4-cyclohexadienone derivatives in enantiomerically pure form.[2,3] In this paper, we describe the intramolecular Diels–Alder reactions of 6-alkenyl-6-(methoxycarbonyl)-2,4-cyclohexadien-1-ones. The resulting tricyclic ring systems contain the β,γ-enone functionality and undergo efficient oxa-di-π-methane photorearrangement.[4] These reactions provide a means for construction of tetracyclic rings of type A (demonstrated for n = 1, 2, and 3) by a process based on C-alkylation of the synthetic equivalence of enolate B. It is anticipated that this chemistry will be of use in the synthesis of polyquinane natural products.[5]



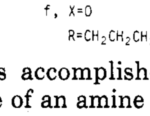
A B

Results and Discussion

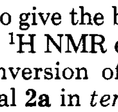
The Birch reduction–alkylation procedure previously described was used to construct 1,4-cyclohexadienes **1a–e** from methyl 2-methoxybenzoate.[1] Reaction of **1a–e** with *N*-bromoacetamide (NBA) in methanol provided bromo ketals **2a–e**.



1a, $R=CH_2CH=CH_2$
b, $R=CH_2CBr=CH_2$
c, $R=CH_2CH_2CH=CH_2$
d, $R=CH_2CH_2CH_2CH=CH_2$
e, $R=CH_2C_6H_4CH=CHCO_2Me$



2



3a–e, $X=(OMe)_2$
f, $X=O$
$R=CH_2CH_2CH_2CH=CH_2$

Dehydrobromination was accomplished by heating bromoketals in the presence of an amine in an aromatic solvent. In most cases, the cyclohexadienone ketals were not obtained (e.g., **3a–c**, **e**), but rather intramolecular Diels–Alder addition occurred to give the bridged adducts directly (e.g., **4a**,**c**, **5a**, and **7a**). ^{1}H NMR evidence for the intermediacy of **3a** in the conversion of **2a** to **4a** was provided by heating bromoketal **2a** in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide. In contrast, cyclohexadienone ketal **3d** was obtained in 76% isolated yield from treatment of **2d** with 1,5-diazobicyclo[4.3.0]non-5-ene (DBN) in refluxing toluene solution (24 h). Tricyclic adduct **6a** could not be obtained from **3d** even at higher reaction temperature (up to ~140 °C). The reluctance of **3d** to undergo Diels–Alder cyclization presumably is a result of unfavorable steric interactions between the developing cyclohexane ring and a ketal methoxyl group. Indeed, **3f**, obtained by ketal hydrolysis of **3d**, underwent smooth cyclization in refluxing toluene solution (7 h) to give **6b** in 95% isolated yield. The remaining

---

[1] Schultz, A. G.; Ditami, J. P.; Lavieri, F. P.; Salowey, C.; Sundararaman, P.; Szymula, M. B. *J. Org. Chem.* **1984**, *49*, 4429.

[2] Schultz, A. G.; Sundararaman, P. *Tetrahedron Lett.* **1984**, *25*, 4591.

[3] Schultz, A. G.; Puig, S. *J. Org. Chem.* **1985**, *50*, 915.

[4] Photochemically generated tricyclo[3.3.0.0^{2,8}]octan-3-ones have been used in polyquinane synthesis: Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. Demuth, M.; Chandrasekhar, S.; Schaffner, K. *J. Am. Chem. Soc.* **1984**, *106*, 1092.

[5] (a) Paquette, L. A. *Top Curr. Chem.* **1979**, *79*, 41. (b) Trost, B. *Chem. Soc. Rev.* **1982**, *11*, 141.

0022-3263/85/1950-3086$01.50/0 © 1985 American Chemical Society