Experimental Section

Reagents.—Toluene, *n*-hexane, and diethyl ether were dried by distillation over $LiAlH_4$ and stored under nitrogen. Norbornadiene (Fluka, practical grade) and butadiene (Phillips, special purity) were used as supplied. Triphenylphosphine (BDH) and other phosphines (Strem) were commercial products. Cobalt and nickel chlorides were dried by treatment with $SOCl_2$. $(i\text{-}C_3H_7)MgCl$ Grignard reagent was prepared from 2-chloropropane (Fluka, practical grade) and Mg turnings. Et_3Al and Et_2AlCl (Fluka, practical grade) were used as supplied.

Oligomerizations.—The reactions were run in glass vials under nitrogen. The reagents were introduced into the reactor in the following order: transition metal compound, ligand (when used), solvent, BD, NBD, and organometallic compound. A small amount of *n*-decane was added as internal standard for quantitative estimations in the glc analysis. The mixture was normally prepared at −78° and kept in a thermostatic bath. At the end of the reaction small amounts of methanol and phenyl-β-naphthylamine were added.

Characterization of the Compounds.—The quantitative composition of the reaction products was determined by glc (C. Erba, Fractovap C, methylsilicone SE 30, P 30–60 mesh, 2 m, 80°, He) on the crude mixture. Isolation of pure C_{11} compounds was accomplished by preparative glc (C. Erba, Fractovap P 100, Apiezon L, Chromosorb W 50–60, 8 m, 220°, He) on fractions enriched by distillation. Spectroscopic characterizations were performed on a Perkin-Elmer 125 ir spectrophotometer (NaCl optics), Varian HA 100-MHz nmr spectrometer (CCl_4, room temperature, TMS reference), and Hitachi RMU 6 E (70 eV, 250°) mass spectrometer.

Anal. Calcd for $C_{11}H_{14}$: C, 90.42; H, 9.58. Found for IV: C, 90.19; H, 9.22. Found for V: C, 90.78; H, 9.61. Physical properties of IV and V: IV, bp 187–189°, $n^{24}D$ 1.4955; V, bp 190–192°, $n^{24}D$ 1.5188.

Registry No.—IV, 28229-18-7; V, 28229-10-9.

Facile Olefin Hydrogenation with Soluble Lithium-Based Coordination Catalysts

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There has been considerable interest in soluble hydrogenation catalysts in recent years. Numerous Ziegler-type catalysts have been developed to effect facile hydrogenation of olefins using alkylaluminum compounds as reducing agents.[1–5] Although Sloan, *et al.*,[1] mention the use of alkyllithiums as reducing agents combined with transition metal salts of groups IV–VIII metals, they prefer alkylaluminums, claiming shorter reduction times. Several patents have also briefly mentioned alkyllithiums as cocatalysts in olefin reductions, but the use of alkylaluminums was preferred.[2–5] We have now found that previous investigators severely underestimated the reactivity of reduction catalysts prepared from alkyllithiums. In our studies Ziegler-type hydrogenation catalysts made from organolithium compounds and transition metal salts of 2-ethylhexanoic acid were fully as active as alkylaluminum-based catalyst systems at convenient concentration levels of catalyst. They are preferable because of the ease of handling of organolithiums compared with alkylaluminums. While these catalysts are generally referred to as soluble, they might exist in a finely divided suspended form. They do not deteriorate when aged for several months.

Active lithium-based hydrogenation catalysts may be prepared by slowly adding a solution of transition metal 2-ethylhexanoate in cyclohexane to a solution of an alkyl- or aryllithium dissolved in cyclohexane or benzene under a nitrogen atmosphere. This catalyst, in the presence of hydrogen, will reduce a variety of cyclic and acyclic olefins, as shown in Table I, utilizing mild conditions of temperature, 50°, and pressure, 50 psi of hydrogen. Cyclic, mono-, and disubstituted acyclic olefins are easily reduced quantitatively in 30 min or less. Trisubstituted olefins such as 1-methylcyclohexene and 2-methylpentene-2 are more resistant to hydrogenation, and the tetrasubstituted olefin 2,3-dimethylbutene-2 is the most resistant. Unsaturation adjacent to an aromatic nucleus is easily hydrogenated, as evidenced by the quantitative reduction of the vinyl group in styrene in 20 min.

TABLE I
HYDROGENATION OF OLEFINS WITH SOLUBLE HYDROGENATION CATALYSTS[a]

Olefin	Catalyst level, mol %	Li/Co	Time, min	% conversion[b]
Cyclooctene	0.6	4.0	30	100
Cyclohexene	0.5	4.0	20	100
Cycloheptene	0.5	3.0	30	100
1-Methylcyclohexene	0.2	6.0	90	44
cis-Pentene-2	0.4	4.0	20	100
Hexene-1	0.5	4.0	20	100
2-Methylpentene-2	0.5	4.0	60	92
trans-Pentene-2	0.4	4.0	30	100
Styrene[c]	0.6	4.0	20	100
2,3-Dimethylbutene-2	0.5	4.0	90	37

[a] Hydrogen pressure, 50 psi; 50°; *n*-butyllithium–cobalt 2-ethylhexanoate cocatalysts. [b] Determined by gas chromatography. [c] Reduction of the vinyl moiety.

The catalytic activity of lithium–cobalt hydrogenation catalysts compares favorably with an aluminum–cobalt catalyst having an aluminum to cobalt ratio (3.3:1) shown by Sloan, *et al.*,[1] to give facile hydrogenations.[6]

The activity of hydrogenation catalysts prepared from alkyl- or aryllithium and transition metal salts of 2-ethylhexanoic acid is a function of the molar ratio of lithium to cobalt (Table II, entries 1–5). At low lithium/transition metal ratios, Li/Co = 1.7, active hydrogenation catalysts are not formed, while at a higher lithium/cobalt ratio, 9.9, hydrogenation activity is greatly diminished. Intermediate ratios give quite active hydrogenation catalysts.

The rate of hydrogenation increases with an increase in catalyst concentration (Table II, entries 6–8). At 0.3 mol % catalyst cyclooctene is rapidly hydrogenated, while at 0.1 mol % catalyst the reaction is slightly slower. At 0.05 mol % catalyst, reduction ceases. The failure to observe hydrogenation of cyclooctene

(1) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963); U. S. Patent 3,113,986 (Dec 10, 1963).
(2) W. R. Kroll, U. S. Patent 3,412,174 (Nov 19, 1968).
(3) French Patent 1,575,046 (June 9, 1969).
(4) Belgian Patent 718,668 (Sept 30, 1968).
(5) S. J. Lapporte, U. S. Patent 3,205,278 (Sept 7, 1965); *J. Org. Chem.*, **28**, 1947 (1963).

(6) A triethylaluminum–cobalt 2-ethylhexanoate catalyst having an Al/Co of 3.3 and at a concentration of 0.3 mol % quantitatively hydrogenated cyclooctene in cyclohexane in 20 min at 50° and 50 psi of hydrogen.

Table II
Hydrogenation of Cyclooctene with Soluble Hydrogenation Catalysts as a Function of Li/Co Ratio and Catalyst Level[a]

Entry	Li/Co[b]	Catalyst level, mol %	Time, min	% conversion
1	1.7	0.3	90	8
2	4.0	0.3	30	100
3	5.6	0.3	20	99
4	6.0	0.3	20	100
5	9.9	0.3	90	16
6	5.6	0.05	90	0
7	5.6	0.1	30	93
8	5.6	0.3	20	99
9	4.7[c]	0.3	90	98

[a] Hydrogen pressure 50 psi, 50°. [b] Molar ratio. [c] *n*-Butyllithium–nickel octoate cocatalysts.

with 0.05 mol % catalyst may be due to loss of catalyst by oxidation or other impurities.

Transition metal salts other than cobalt 2-ethylhexanoate may be used as cocatalysts in the hydrogenation of olefins. Nickel 2-ethylhexanoate–*n*-butyllithium hydrogenation catalyst is less active than its cobalt counterpart (Table II, entry 9).

A number of alkyl- or aryllithiums have been used in place of *n*-butyllithium as cocatalysts with cobalt 2-ethylhexanoate in the hydrogenation of olefins. Comparative data at 50°, 50 psi of hydrogen pressure, Li/Co = 4.0, are listed in Table III. Similar reactivity is observed with aromatic and primary and secondary alkyllithiums. Hydrogenation activity is diminished significantly if cyclopentyllithium is used as the cocatalyst, but this may reflect the unknown purity of cyclopentyllithium.

Table III
Hydrogenation of Olefins with Soluble Hydrogenation Catalysts as a Function of Lithium Source[a]

Lithium source	Olefin	Time, min	% conversion
n-Butyllithium	*cis*-Pentene-2	20	100
Ethyllithium	Cyclooctene	10	100
sec-Butyllithium	Cyclooctene	10	100
Cyclopentyllithium	Cyclooctene	90	63
Phenyllithium	Hexene-1	10	100

[a] Hydrogen pressure 50 psi, Li/Co = 4.0, 50°, 0.3 mol % catalyst.

Cycloolefins may be selectively reduced in the presence of their 1-methyl counterparts. Cyclohexene in a 50% mixture of cyclohexene and 1-methylcyclohexene is quantitatively reduced in 10 min while 18% reduction of 1-methylcyclohexene occurs. A *n*-butyllithium–cobalt 2-ethylhexanoate catalyst was used having a Li/Co of 6.0 at a 0.2 mol % catalyst level at 50°, 50 psi of hydrogen pressure. In an analogous experiment with a 50% mixture of cycloheptene and 1-methylcycloheptene, cycloheptene is quantitatively reduced in 10 min while 25% reduction of the 1-methyl derivative occurs. The selectivity is not absolute and higher ratios of Li/Co may show improved selectivity.

An active soluble lithium-based hydrogenation catalyst system has been discussed in terms of several reaction parameters. This catalyst system is as active as aluminum-based systems at convenient catalyst concentrations and offers as an advantage the ease of handling of organolithiums compared with other hydrogenation catalysts such as alkylaluminums.

Experimental Section

Materials.—Aryl- and alkyllithium reagents were purchased from the Foote Chemical Co. A solution of cobalt 2-ethylhexanoate in cyclohexane was purchased from the Harshaw Chemical Co. and nickel 2-ethylhexanoate was purchased from K & K Laboratories. The olefins were purchased from either the Eastman Kodak Co. or the Aldrich Chemical Co. and were distilled and stored over molecular sieves prior to use. Solvents were passed through molecular sieves. All reactions and reagent transfers were carried out under a dry nitrogen atmosphere.

Catalyst Preparation.—A 0.285 *M* solution of catalyst (molarity based upon the amount of lithium) was prepared by adding 14.1 g of cobalt 2-ethylhexanoate solution (12.0% cobalt, w/w) over a period of 90 min to a solution of 0.0854 mol of *n*-butyllithium in 287 ml of cyclohexane; Li/Co = 3.0. Other ratios were prepared in the same manner.

Olefin Hydrogenation.—In a typical example, cycloheptene (44.9 g) was dissolved in 1500 ml of cyclohexane and placed with 0.5 mol % of a *n*-butyllithium–cobalt 2-ethylhexanoate catalyst having a lithium/cobalt ratio of 3.0:1 in a 2-l. reactor thermostated at 50°. The reactor was kept at a constant hydrogen pressure of 50 psi throughout the hydrogenation. Aliquots of the reaction mixture were withdrawn periodically, and the per cent conversion was determined by measuring the amounts of cycloheptane and cycloheptene using a F & M Dual Flame Model 810 gas chromatograph with an activated alumina column at 200°.

Registry No.—Cyclooctene, 931-88-4; cyclohexene, 110-83-8; cycloheptene, 628-92-2; 1-methylcyclohexene, 591-49-1; *cis*-pentene-2, 627-20-3; hexene-1, 592-41-6; 2-methylpentene-2, 625-27-4; *trans*-pentene-2, 646-04-8; styrene, 100-42-5; 2,3-dimethylbutene-2, 563-79-1; *n*-butyllithium, 109-72-8; cobalt 2-ethylhexanoate, 136-52-7; nickel octanoate, 4995-91-9; ethyllithium, 811-49-4; *sec*-butyllithium, 598-30-1; cyclopentyllithium, 23473-12-3; phenyllithium, 591-51-5.

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The Deconjugation of Isophorone[1]

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We were interested in an efficient procedure for the deconjugation of isophorone (**1**) to β-phorone (**2**) in connection with our recent synthesis of an allenic sesquiterpene.[2] While Kharasch and Tawney[3] have described a procedure for accomplishing this transformation, we found that the results were disappointingly erratic, giving sometimes large amounts of viscous, black material and sometimes a mixture of two crystalline products.

(1) Supported by NIH Training Grant 5RO1 GM00834-09.
(2) J. Meinwald and L. Hendry, *Tetrahedron Lett.*, 1657 (1969).
(3) M. S. Kharasch and P. O. Tawney, *J. Amer. Chem. Soc.*, **63**, 2308 (1941).