ethyl acetate was attempted but compound **15** could not be isolated in pure form.

Monomethylation of 1a. A mixture of 4.69 g (18.0 mmol) of **1** and 7.66 g (54.0 mmol) of CH_3I was dissolved in 35 mL of DMF, cooled to 0 °C, and stirred under nitrogen. After 30 min, 0.76 g of sodium hydride, 60% dispersion (19.0 mmol), was added in one portion. The reaction was continued for 5 h at 0 °C and 5 h at room temperature. After quenching into ice water and workup as above, the crude yield of a dark brown gum was 5.15 g (>100%). Recrystallization of the crude product from ethanol afforded 1.70 g (34%) of a dark brown solid, which was recrystallized 3 times from ethanol to afford pure **16**, mp 167–168 °C. ^1H NMR: δ 1.55 (d, J = 6 Hz, 3 H, methyl), 3.65 (m, 1 H, quinolyl H_4), 6.62 (d, J = 6 Hz, 2 H, quinolyl H_3), 7.0–7.5 (m, 9 H). Irradiation of the doublet at 1.55 ppm caused collapse of the multiplet at 3.65 ppm to a doublet (J = 6 Hz). Mass spectrum, m/z:274 (molecular weight, 274.32). Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: 78.70; H, 5.16; N, 10.24.

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A New, Convenient Preparation of Bis(1,5-cyclooctadiene)nickel(0)

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Bis(1,5-cyclooctadiene)nickel(0), $Ni(COD)_2$, is an important and useful complex of interest as a starting material for the synthesis of other organonickel complexes and as a catalyst for a number of nickel-catalyzed organic transformations.[1] In connection with our studies of the allylnickel chemistry of 2-alkenyl-1,3-dioxolanones,[2] we required a convenient, large-scale preparation of $Ni(COD)_2$. Since the standard procedures[3-5] for preparing $Ni(COD)_2$ proved cumbersome and inconvenient in our hands, a new, streamlined protocol was developed. Herein, we report the details of a modified synthesis of $Ni(COD)_2$ which greatly simplifies its preparation.

The standard procedure for the synthesis of $Ni(COD)_2$, as developed by Wilke[3] and modified by Semmelhack[4] and Schunn,[5] involves the reduction of bis(acetylacetonate)nickel(II), $Ni(acac)_2$, with triethylaluminum in the presence of 1,5-cyclooctadiene and 1,3-butadiene (eq 1).

$$\mathrm{Ni(acac)_2 + 2AlEt_3 + 2\,1,5\text{-}COD \xrightarrow[\substack{0\text{–}25\ ^\circ C\\ \text{butadiene}}]{\text{toluene}} Ni(COD)_2} \qquad (1)$$

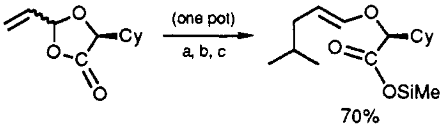
Inasmuch as it seems likely that the nickel(0) product is formed via reductive elimination from a bis(hydrido)nickel(II) or (ethyl)(hydrido)nickel(II) intermediate, we reasoned that a simpler and perhaps higher yielding preparation[6] of $Ni(COD)_2$ would result from the direct formation of a bis(hydrido)nickel(II) intermediate through the use of a hydride reducing agent such as diisobutylaluminum hydride (DIBAH). Literature precedents for this strategy are found in the work of Julia[7] and Schwartz[8] who generated low-valent nickel catalysts in situ via DIBAH reduction of $Ni(acac)_2$.

In the event, dropwise treatment of a slurry of technical grade (90%) $Ni(acac)_2$ in tetrahydrofuran (THF) with a THF solution of DIBAH at −78 °C in the presence of 1,5-cyclooctadiene led to rapid reaction (eq 2). After the addition was complete, the dark, reddish-brown solution was allowed to warm to 0 °C over a 1-h period and then diluted with diethyl ether to give a yellow precipitate. The precipitation was completed by cooling the suspension at −78 °C for 12 h. The product was isolated by filtration at −78 °C to give a 65–75% yield of $Ni(COD)_2$ as a yellow-green powder. The crude material so obtained was determined to be of sufficient purity for most applications.[9]

$$\mathrm{Ni(acac)_2 + 2.5Bu_2AlH + 4\,1,5\text{-}COD \xrightarrow[-78\text{ to }0\ ^\circ C]{\text{THF}} \underset{65\text{–}70\%}{Ni(COD)_2}} \qquad (2)$$

This procedure offers a number of advantages over previous methods of $Ni(COD)_2$ synthesis. Firstly DIBAH is a much more commonly employed reducing agent, and is more easily handled, than triethylaluminum. Secondly, the use of technical grade $Ni(acac)_2$ instead of the more expensive high purity form greatly reduces the cost of the procedure without affecting the yields or purity of the product. Thirdly, the butadiene additive employed in the triethylaluminum procedures is omitted in this protocol without adverse effects. Fourthly, whereas existing procedures[3-5] require the collection of multiple crops of product to achieve good yields, the DIBAH method gives good yields in a single isolation. Furthermore, the purity of the $Ni(COD)_2$ product is such that no additional purification steps are required for most applications.[9]

The last two features of the new procedure are conducive to the development of one-pot reaction schemes which avoid the isolation of air-sensitive intermediates. An example is the allylnickel-based, one-pot homoenolate anion equivalent reaction developed in these laboratories (eq 3, Cy = cyclohexyl).[10] Although this procedure is simply a combination of previously developed, stepwise procedures,[10] the one-pot protocol significantly facilitates application of the allylnickel homoenolate equivalent chemistry. Extensions of this approach to other nickel-mediated reactions should also be possible and allow for the more widespread application of such chemistry.



(3)

(a) $Ni(COD)_2$ (prepared in situ from $Ni(acac)_2$/DIBAH/COD); (b) MeSiCl; (c) i-PrI, DMF/C_6H_6, $h\nu$.

Experimental Section

All manipulations were performed under a purified nitrogen atmosphere using standard air-free techniques in a glovebox or on a dual-manifold Schlenk line. Tetrahydrofuran, diethyl ether,

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[1] Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel, Vol. I and II*; Academic Press: New York, 1974.

[2] Krysan, D. J.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 6273.

[3] Bogdonavich, B.; Kroner, M.; Wilke, G. *Ann.* **1966**, *699*, 1.

[4] Semmelhack, M. F. *Org. React.* **1972**, *19*, 115.

[5] Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

[6] The triethylaluminum procedures[3-5] involve extended reaction times at 25 °C. In view of the thermal sensitivity of the product, it seemed plausible that reaction at lower temperatures would result in higher yields and/or more pure product.

[7] Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1986**, *o17*, 383.

[8] Hansen, R. T.; Carr, D. B.; Schwartz, J. *J. Am. Chem.* Soc. **1978**, *100*, 2244.

[9] If high purity material is required, the crude product can be purified by recrystallization from toluene (see the Experimental Section).

[10] (a) Procedures for the stepwise allylnickel homoenolate chemistry have been published.[2] Full details of the one-pot homoenolate chemistry will be published shortly.[b] (b) Krysan, D. J.; Sabat, M.; Mackenzie, P. B., manuscript in preparation.

and toluene were vacuum transferred from Na/benzophenone ketyl and stored under nitrogen before use. Technical grade (90%) bis(acetylacetonate)nickel(0) and 1.0 M solutions of diisobutylaluminum hydride (DIBAH) in tetrahydrofuran were obtained from Aldrich and used as received. 1,5-Cyclooctadiene (redistilled grade) was obtained from Aldrich and freeze–pump–thaw degassed (three cycles) prior to use; 90-MHz ^{1}H NMR spectra were recorded on a 90-MHz JEOL FX-90 instrument and were referenced to tetramethylsilane.

Bis(1,5-cyclooctadiene)nickel(0). A 250-mL Schlenk flask equipped with a stir bar and a pressure-equalizing addition funnel was charged with technical grade bis(acetylacetonate)nickel(II) (4.67 g, 0.0182 mol, 1.00 equiv) and briefly dried under vacuum with a heatgun. After cooling and establishing a positive nitrogen atmosphere, the solid was suspended in tetrahydrofuran (25 mL) and treated with 1,5-cyclooctadiene (7.93 g, 0.0723 mol, 4.00 equiv). The suspension was cooled to −78 °C with a dry ice/acetone bath to give a green slurry. A 1.0 M solution of DIBAH (45.4 mL, 0.0454 mol, 2.50 equiv) in tetrahydrofuran was transferred to the addition funnel under nitrogen via a cannula. The DIBAH solution was added over 1 h to give a dark, reddish brown solution which was allowed to warm to 0 °C over a 1-h period. The solution was treated with diethyl ether (65 mL) to give a light yellow precipitate. The suspension was cooled to −78 °C and allowed to stand for 12 h to complete precipitation. The solid product was isolated by filtration at −78 °C via a filter paper tipped cannula, washed with cold diethyl ether (15-mL portions) until brown residues were removed, and dried in vacuo. $Ni(COD)_2$ was obtained as a pale yellow powder (3.2 g, 72%) and was suitable for immediate use. 90-MHz ^{1}H NMR (C_6D_6): δ 4.28 (8 H, broad singlet), 2.10 (16 H, broad singlet).

Recrystallization of Bis(1,5-cyclooctadiene)nickel(0). In a glovebox, crude $Ni(COD)_2$ (3.2 g) was dissolved in a minimum volume of toluene (ca. 25 mL/g) at 25 °C and rapidly filtered through Celite to remove metallic nickel. The deep yellow solution was allowed to stand at −78 °C for 12 h to give bright yellow-orange needles. Removal of the supernatent at −78 °C through a filter paper tipped cannula, followed by pentane wash (2 × 15 mL), gave pure material (1.28 g, 40% recovery).

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Registry No. $Ni(COD)_2$, 1295-35-8; $Ni(acac)_2$, 3264-82-2.

Additions and Corrections

Vol. 54, 1989

John J. Chapman* and Jack R. Reid. An Electrophile-Assisted Nonsolvent Synthesis of Alkyl Macroisocyclic Ethers: An Improved Nonsolvent Williamson Synthesis of Medium-Sized Alkyl Carbocyclic Ethers.

Page 3757, column 2, lines 23–28, should read as follows. Nonsolvent ether syntheses utilizing aliphatic alcohols in one study and easily reacted aromatic species in another, with either KOH or NaOH in the presence of 2 mol % of Aliquat 336, were recently reported by Loupy et al.[23,31] Many of the reported products have alternatively been prepared in solvent systems with little or no apparent difficulties.[4,13-16,21,24]

Page 3758. We failed to cite the paper by Barry et al. [Barry, J.; Bram, G.; Decodts, G.; Loupy, A.; Pigeon, P.; Sansoulet, J. "Alkylations en Absence de Solvant Organique-3: Preparation D'ethers Aliphatiques par Alkylation des Alcoolates Dans des Conditions Douces et Economiques". *Tetrahedron* **1984**, *40*, 2945]. This paper should be listed as ref 31. We apologize for this omission.

Page 3759, column 1, line 18. Cyclododecanol should be deleted and replaced by cyclotetradecanol.

Page 3759, column 1, line 26. Cyclododecanol should be deleted and replaced by cyclopentadecanol.