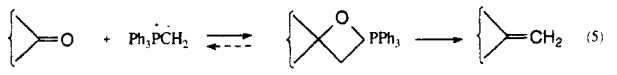
reagents, but of steric hindrance to rehybridization. If the rate-determining transition states occur after the sp^2-hybridized ketones have begun to rehybridize toward sterically more demanding sp^3 intermediates, the energy of the transition states could be quite high.

Inspection of models suggests that the phenyl rings are very close to the carbonyls and would restrict movement of the oxygen atom during rehybridization. Formation of the *syn*-alcohols from the *exo*-8-ketone 1, for example, would require increased distance between the C-8 bridge and the *syn*-phenyl, and thus molecular reorganization must occur. The potentially reversible additions of phosphorus ylides[11d] would be sensitive to such constraints (eq 5). The decreased reactivity of these ketones constrasts with that of ditriptycyl ketone where low reactivity[12] is caused by hindrance to reagent approach not rehybridization.



The lower IR absorption of the carbonyl group in the diphenyl-*exo*-8-ketone 1 (1750 cm^{-1}) in comparison to the unsubstituted *exo*-8-ketone (1794 cm^{-1})[13] suggests that π overlap with the proximate phenyl ring has diminished the electrophilic nature of the carbonyl group, thus rendering it less reactive to less nucleophilic reagents.

The reactions of the *exo*-8-ketone 1 with lithium aluminum hydride and methyllithium must involve earlier transition states that are less affected by steric problems of rehybridization. These bridged ketones with proximate phenyls appear to be good probes of transition-state timing in carbonyl additions.

Experimental[14] Section

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-*syn*-8-ol.** To *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-en-*syn*-8-ol[5] (516 mg, 2.0 mmol) in 20 mL of methanol, under nitrogen, in a three-necked flask fitted with a condenser and a barium hydroxide trap, was added freshly prepared potassium azodicarboxylate[15] (0.75 g, 3.9 mmol) with stirring. A solution of glacial acetic acid (0.4 mL in 5 mL of methanol) was then added dropwise over a period of 30 min, and stirring was continued for 1 h. Then, 100 mL of cold water was added and the mixture was repeatedly extracted with hexane. The hexane solution was dried ($MgSO_4$). Concentration afforded the desired *endo-syn*-8-alcohol as a white solid: 480 mg (87%); mp 204-205 °C; ^1H NMR δ 7.03-7.90 (10 H, m, ArH), 4.30 (1 H, br s, H_8), 2.38 (2 H, br s, $H_{1,5}$), 2.13-2.33 (3 H, m, $H_{2,4}$ and OH), 1.23 (4 H, br s, $H_{6,7}$); IR 3500-3380, 2980, 1600, 1500, 1450, 1410 cm^{-1}; ^{13}C NMR δ 141.9 (Ar ipso), 125.96, 126.51, 127.39, 127.60, 128.41, 130.80 (Ar), 96.03 (C_8), 58.75 (C_3), 43.20 ($C_{1,5}$), 32.22 ($C_{2,4}$), 22.46 ($C_{6,7}$). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.89; H, 7.26.

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-8-one (5).** Pyridinium chlorochromate oxidation[16] of 138 mg (0.5 mmol) of the *endo-syn*-8-alcohol produced 113 mg (83%) of ketone 5: mp 173.5-174.5 °C; ^1H NMR δ 7.03-7.87 (10 H, m, ArH), 2.63 (2 H, br s, $H_{1,5}$), 1.93 (2 H, t, J = 3 Hz, $H_{2,4}$), 1.4 (4 H, s, $H_{6,7}$); IR 3000, 1770, 1600, 1500, 1450 cm^{-1}; ^{13}C NMR δ 199.69 (C=O), 148.79, 140.61 (Ar ipso), 126.42, 126.94, 127.61, 127.81, 128.59, 130.48 (Ar), 46.47 (C_3), 41.12 ($C_{1,5}$), 20.45 ($C_{2,4}$), 19.64 ($C_{6,7}$). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.57; H, 6.65.

8-Methylene-*endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane (6). In a flame-dried, three-necked flask, equipped with a magnetic stirrer and a reflux condenser, under nitrogen was placed triphenylmethylphosphonium bromide (680 g, 1.95 mmol) along with 30 mL of anhydrous ether. Standardized *n*-butyllithium[17] (1.8 mL, 1.95 mmol) was introduced by syringe through a septum while the flask was kept at 0 °C and the mixture was stirred for 1.5 h. To the yellow suspension of the ylide was added a solution of 5 (180 mg, 0.65 mmol) in 5 mL of anhydrous ether. After overnight reflux, 20 mL of cold water was carefully added until the precipitate completely dissolved, and the resulting solution was extracted with ether. The ether solution was dried ($MgSO_4$), concentrated, and subjected to rotational TLC with hexane-ether eluent. The alkene 6 (100 mg, 57%) was obtained as white crystals: mp 152-153.5 °C; ^1H NMR δ 6.97-7.83 (10 H, m, ArH), 4.23 (2 H, s, H_9), 2.77 (2 H, br s, $H_{1,5}$), 1.97 (2 H, t, J = 3 Hz, $H_{2,4}$), 1.27 (4 H, br s, $H_{6,7}$); IR 3020, 2980, 1685, 1600, 1500, 1450 cm^{-1}; ^{13}C δ NMR 140.76, 150.23 (Ar ipso), 125.78, 126.46, 127.33, 127.57, 128.26, 130.94 (Ar), 167.28 (C_8), 89.50 (C_9), 55.12 (C_3), 42.23 ($C_{1,5}$), 31.24 ($C_{2,4}$), 24.32 ($C_{6,7}$). Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.25; H, 7.58.

6-Methylene-*exo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane (4). The procedure used to prepare 6 was applied to *exo*-6-ketone 3 to afford white crystals (120 mg, 68%) of alkene 4: mp 81.5-83.5 °C; ^1H NMR δ 7.35 (5 H, pseudo s, ArH), 7.23 (5 H, pseudo s ArH), 4.90 (1 H, s, H_{9a}), 4.60 (1 H, s, H_{9b}), 2.95 (1 H, s, H_5), 2.60 (1 H, s, H_1), 2.10 (1 H, s, H_7), 1.60 (2 H, s, $H_{2,4}$), 0.65 (2 H, s, H_8); IR 3000, 2950, 1680, 1600, 1500, 1450 cm^{-1}. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.57; H, 7.43.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, the Arthur Schmitt Foundation for Fellowships to M.P. and R.S., and Milind Choubal for assistance with the drawings.

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Regioselectivity in the Alkylation of Ambident Anions of 1-Acyl-1,2-dihydroquinaldonitriles (Quinoline Reissert Compounds)

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Introduction

Structure 1 is a 1-acyl-1,2-dihydroquinaldonitrile or quinoline Reissert compound. By virtue of the acidity of the proton α to the cyano group this class of compounds can be elaborated with a number of electrophiles such as alkyl halides. Such reactions make Reissert compounds valuable synthetic intermediates.[1]

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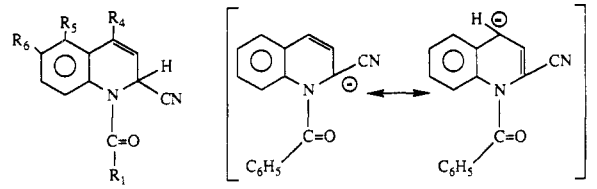
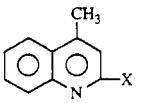


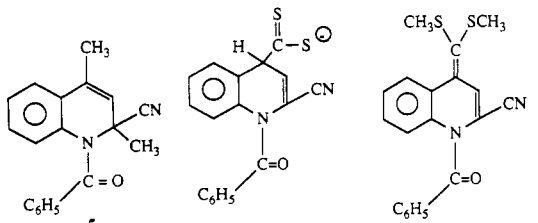
2

1: R_1=C_6H_5, R_4=R_5=R_6=H
3: R_1=C_6H_5, R_4=CH_3, R_5=R_6=H
9: R_1=C_6H_5, R_4=R_5=H, R_6=CH_3
10: R_1=C_6H_5, R_4=R_6=CH_3, R_5=H
12, R_1=OC_2H_5, R_4=H, R_5, R_6=benzo

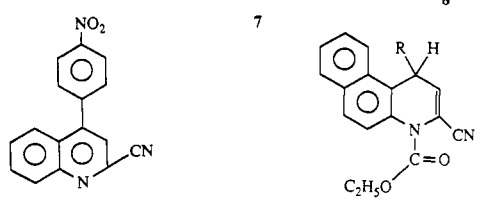


4, X=H
6, X=CH_3

Boekelheide and Weinstock reported that reaction of the ambident anion **2** derived from **1** using phenyllithium in dioxane–ether with methyl iodide produced lepidine (**4**) after basic hydrolysis of presumed intermediate **3**.[2] They also reported that methylation of the lepidine Reissert compound **3** via its anion yielded 47% of **5**, which by hydrolysis provided 2,4-dimethylquinoline (**6**). Mass balance in the experiments leading to **4** was not good; intermediate **3** was obtained in only 29% yield. The reported melting point of **3** was more than 10° lower than that later reported by Popp, Blount, and Melvin.[3] The hydrolysis product **4** was obtained as an oil in 62% yield and identified by preparation of its picrate in unspecified yield. Similarly, no yield was reported for hydrolysis of **5** to **6**, which was identified via the picrate prepared in unspecified yield.



5 7 8

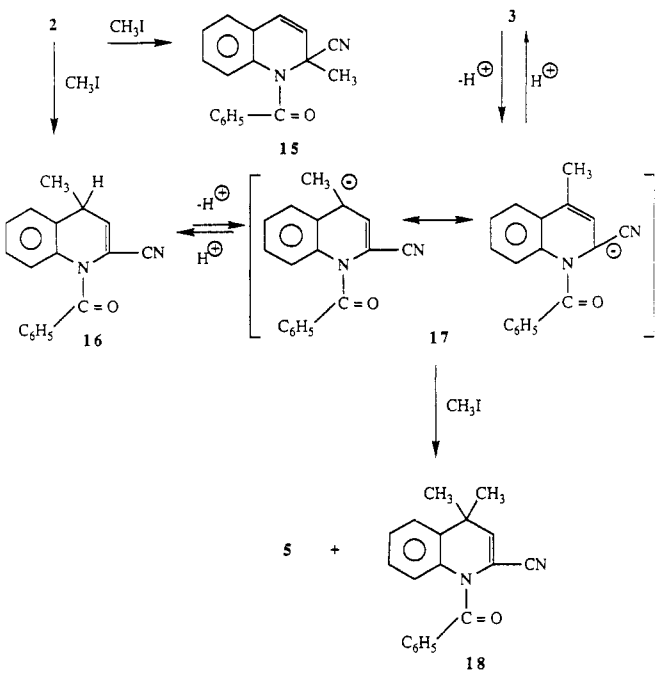


11 13, R=H 14, R=CH_3

Popp and Wefer reported that anion **2** (NaH/DMF) treated first with CS_2 and then methyl iodide gave a nearly quantitative yield of **8** presumably via intermediate **7**.[4] Popp and Wefer report an attempt to use NaH/DMF for methylation, but obtained "a dark messy reaction mixture".[5]

Later, Uff and co-workers reported that alkylation of the anion of **9**, formed with NaH/DMF, produced 40% of the 4-methyl product **10**.[6] Arylation of **1** using NaH/DMF with *p*-nitrofluorobenzene afforded the 4-product **11** in 47% yield after chromatographic purification.[7]

Scheme I



15 16 17 18

Finally Popp and co-workers were able to obtain the urethane **12** and its 1,4-dihydro isomer **13**.[8] Methylation of **12** (NaH/DMF) produced the 1,4-dihydro product **14** in 78% yield. Compound **13** also gave **14** in unspecified yield.[8]

Based on the poor mass balances and some apparent contradictions among some of the above mentioned reactions, we decided to undertake a reinvestigation of the regioselectivity of the methylation of the anions of **1** and **3** using modern NMR techniques.

Results and Discussion

Scheme I outlines the possible methylation reactions of anion **2** and subsequent base-promoted methylations. Clearly a number of possible alkylation products are possible in addition to **3**; the other possible alkylated products are **15** formed by methylation at the 2-position, the 4-methylated 1,4-dihydro intermediate **16**, and dimethyl derivatives **5** and **18** formed by methylation of the ambident anion **17** derived from **16** and **3**. In order to study these possibilities, we utilized Reissert compounds **1** and **3**. The latter was prepared directly from lepidine (**4**). Compound **3** has mp 169–170 °C as reported by Popp, Blount, and Melvin,[3] but in contrast to the value 159.0–161.5 °C reported by Boekelheide and Weinstock.[2]

Methylation of **3** via its anion **17** (prepared with NaH/DMF) with excess methyl iodide produced the new compounds **18** and **5** in 43 ± 3% and 57 ± 3% yields, respectively, which are the average results of three runs. The crude reaction products were analyzed by proton NMR. Compounds **5** and **18** were isolated in pure form to be used as standards for the analysis. Pure **5** has mp 136–137 °C. Most significant in its NMR spectrum are the methyl signals at δ 1.84 (2-CH_3, singlet) and 2.19 (4-CH_3, doublet, J = 1.5 Hz coupling with H_3). Pure **18** has mp 134–5 °C and in its proton NMR spectrum a six-proton

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singlet due to the geminal methyls appears at δ 1.55.

Armed with a knowledge of the regioselectivity of methylation of intermediate ambident anion 17 derived from 16 and/or 3, we set out to determine the regioselectivity of methylation of ambident anion 2. This was done using two stoichiometries.

First we treated Reissert compound 1 with 2 equiv of base and an excess of methyl iodide. Thus, it was expected that all of intermediate 16 that formed would be converted to 5 and 18 via ambident anion 17. Furthermore, the same ratio of 5 to 18 as obtained from 3 via 17 was expected. Any 15 produced by methylation of 2 at the 2-position was not expected to react further. NMR analysis of the reaction mixture showed in addition to 5 and 18 in the expected ratio (40:60 ± 2 as determined by integration of the methyl signals at δ 1.84 and 2.19 vs. 1.58) a fourth methyl singlet at δ 1.88. This latter signal is attributed to the 2-methyl product 15. Since no other methyl signals were observed, methylation of 1 in the presence of 2 equiv of base initially produced 16 ± 2% of 2-methyl product 15 and 84 ± 2% of 4-methyl product 16. Attempts to prepare 15 from 2-methylquinoline by treatment with benzoyl chloride and trimethylsilyl cyanide failed.

The second stoichiometry employed was 1 equiv of base relative to Reissert compound 1 in the presence of excess methyl iodide. In good agreement with the above-described experiment, 11 ± 4% of the product was 15. The second methylation of intermediate 4-methyl compound 16 via ambident anion 17 occurred to the extent of 52 ± 4% at the 2-position and 48 ± 4% at the 4-position, yielding 5 and 18 (11% and 10%), respectively. Also 52% of the new 1,4-dihydro compound 16 was isolated. In the proton NMR spectrum of 16, irradiation of the methyl doublet at δ 1.53 causes the H_4 multiplet at δ 3.65 to collapse to a doublet (residual coupling with H_3). Compound 16 has mp 167–168 °C, very close to that of its isomer 3 (169–170 °C). It is possible that Boekelheide and Weinstock isolated a mixture of 3 and 16, thereby accounting for the low melting point (159–161.5 °C) in spite of an acceptable elemental analysis. By NMR 16 ± 5% of 1 remained unreacted, giving a good mass balance.

These results confirm the oft-quoted but unsubstantiated claim that ambident anion 2 is methylated at the 4-position in preference to the 2-position (~84:16) in agreement with results reported for formation of 8,[4] 11,[7] and 14.[8] But, contrary to the view of Uff et al.[6] based upon Boekelheide and Weinstock's report[2] that "it was considered unlikely that a structure of type 18 would result" from a Reissert compound with a "blocking group at its 4-position", methylation of 3 occurs almost equally at the 4-position (48%) to form the 4,4-dimethyl-1,4-dihydro compound 18 and at the 2-position to produce 5 (52%). This probably accounts for the low yields of 2-alkylated products reported by Uff et al. for 10 and analogues.[6] The yield of 5 by methylation of 3 corresponds roughly with Boekelheide and Weinstock's report[2] (47%), although they apparently did not detect the interesting *gem*-dimethyl product 18 that forms to nearly the same extent. Basic hydrolysis of 18 would not aromatize the pyridine ring and hence no picrate could be isolated from that product, consistent with the report of Boekelheide and Weinstock.[2]

Elsewhere[9] we have rationalized the preference for 4-methylation of anion 2 in terms of hard–soft acid–base concepts. Alkylation of anion 17 presumably reflects the steric constraints imposed by the 4-methyl substituent. Because of their effects on "hardness" other solvent/base systems may provide different regioselectivities.

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Summary

Methylation of the ambident anion of the quinoline benzoyl Reissert compound (1) occurs regioselectively (84%) at the 4-position with NaH/DMF and 16% at the 2-position. However, subsequent methylation of the 4-methylquinoline (lepidine) Reissert compound (3) takes place surprisingly with only slight regioselectivity for the 2-position (52%) versus the 4-position (48%). The latter reaction produces a *gem*-dimethyl-1,4-dihydroquinoline derivative (18), which was not previously detected by other workers.

Experimental Section

Melting points were determined in a Thomas-Hoover hot oil capillary melting point apparatus and are corrected. The IR spectra were determined in KBr pellets on a Nicolet MX-L FTIR spectrophotometer. The NMR spectra were recorded on a Brucker 270-MHz FT instrument in $CDCl_3$ with TMS as internal standard. In all spectra, the relaxation delay was set at 2.0 s. The product compositions were determined by performing two integrations per crude sample. The total integral for the methyl region was adjusted to full scale (25 cm). Individual peaks were evaluated by physical measurement of integral signal heights. The uncertainly in an individual percentage is estimated to be 2%. For each chemical reaction, e.g., methylation of 1 with 2 mol of base, two to four independent syntheses were carried out. Values cited for product distributions are averages. Standard deviations are reported. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were determined on a VG Analytical 7070 EMS instrument. DMF was dried over calcium hydride prior to use.

***N*-Benzoyl-1,2-dihydroquinaldonitrile (1) and *N*-Benzoyl-4-methyl-1,2-dihydroquinaldonitrile (3).** These compounds were prepared via the methylene chloride/water method using quinoline for 1 and lepidine for 3, following the procedure of Popp, Blount, and Melvin.[3] The yields were 78% and 63%, respectively.

Methylation of 1. A mixture of 1.92 g (7.0 mmol) of 1 and 2.98 g (21.0 mmol) of methyl iodide was allowed to stir in 25 mL of DMF for 30 min at 0 °C under nitrogen. Sodium hydride (0.367 g of 55% dispersion, 8.4 mmol) was added in one portion. The resulting yellow mixture was allowed to stir at 0 °C for 4 h, followed by 4 h at room temperature. The mixture was poured over crushed ice and extracted with dichloromethane. The extract was washed 3 times with water and dried over magnesium sulfate. Removal of solvent afforded 1.67 g of dark brown gummy solid (83%). TLC of the crude product using dichloromethane/silica gel revealed two spots, $\Delta R_f < 0.1$. Flash chromatography using dichloromethane/silica gel yielded 0.4 g (20%) of 5 and 0.4 g (20%) of 18. Compound 5 was obtained pure from the column, mp 136–7 °C. ^{1}H NMR: δ 1.84 (s, 3 H, 2-methyl protons), 2.19 (d, J = 1.5 Hz, 3 H, 4-methyl protons), 5.88 (d, J = 1.5 Hz, 1 H, quinolyl H_3), 6.45 (dd, J = 8 Hz, 1 Hz, 1 H, quinolyl H_5), 6.85 (td, J = 8 Hz, 1 Hz, 2 H, quinolyl H_6), 7.02 (td, J = 8 Hz, 1 Hz, 2 H, quinolyl H_7), 7.2–7.5 (5 H), 7.58 (dd, J = 8 Hz, 1 Hz, 2 H, aroyl 2,6 protons). Compound 18 was recrystallized from ethanol, mp 134–5 °C. ^{1}H NMR: δ 1.55 (s, 6 H, *gem*-dimethyl), 6.47 (s, 1 H, quinolyl H_3), 7.0–7.5 (m, 9 H). Anal. Calcd for: $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 78.75; H, 5.57; N, 9.67.

Dimethylation of 1. A mixture of 2.60 g (10.0 mmol) of 1 and 8.52 g (60.0 mmol) of methyl iodide in 30 mL of dry DMF was cooled to 0 °C and stirred under nitrogen for 30 min. Then 0.96 g of sodium hydride, 55% dispersion (22 mmol), was added in one portion. The reaction was continued 4 h at 0 °C and 4 h at room temperature. The mixture was poured over crushed ice and extracted with dichloromethane. The organic layer was washed 5 times with water and dried over magnesium sulfate. Removal of solvent afforded 3.13 g (100%) of a dark brown gum. Analysis of the crude product via ^{1}H NMR showed the absence of 1 and 3, peaks of 5 at 1.84 ppm and 2.19 ppm, the methyl peak of 18 at 1.55 ppm, and a singlet at 1.88, which was assigned to 15. Column chromatography using gravity silica and 80:20 hexane/

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. ^{1}H 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.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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).

$$Ni(acac)_2 + 2AlEt_3 + 2\,1,5\text{-COD} \xrightarrow[\text{butadiene}]{\text{toluene}} Ni(COD)_2 \quad (1)$$

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 $Ni(acac)_2$.

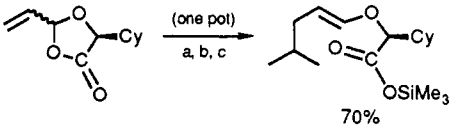
In the event, dropwise treatment of a slurry of technical grade (90%) $Ni(acac)_2$ in tetrahydrofuran (THF) with a THF solution of DIBAH at −78 °C in the presence of 1,5-cyclooctadiene led to rapid reaction (eq 2). After the

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

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]

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



70% (3)

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

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.

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,

(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.