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Electron Transfer in Nickel-Catalyzed Addition Reactions of Organozirconium Compounds to Unsaturated Ketones

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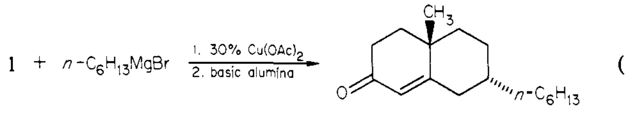
Abstract: The species formed by reacting $Ni(acac)_2$ with 1 equiv of Dibah have been studied with regard to their ability to catalyze carbon–carbon bond-forming reactions involving organozirconium compounds. Catalytic activity for these species is noted upon mixing the nickel and aluminum reagents; activity falls to almost nil after 24 h. Gas evolution studies monitoring the formation of isobutane suggest that these catalytically active species involve Ni(I). Cyclic voltammetric measurements and comparative investigations involving oxidative addition of aryl halides suggest that these catalyst species are good electron-transfer reagents. A mechanism for nickel-catalyzed conjugate addition of alkenylzirconium reagents to α,β-enones is proposed which involves one-electron reduction of the substrate by the Ni(I) catalyst. Comparisons between nickel-catalyzed and copper-catalyzed addition reactions of organometallics to conjugated dienones are described.

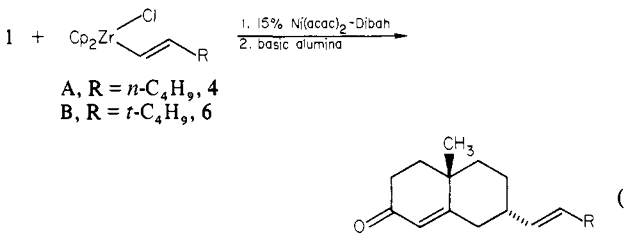
Introduction

We recently described the nickel-catalyzed conjugate addition of alkenylzirconium or alkynylaluminum reagents to α,β-unsaturated ketones.[1,2] To examine the scope of these nickel-catalyzed procedures, we investigated reactions using dienones as substrates[3-6] for addition of alkenylzirconium species. Addition reactions using the $Ni(acac)_2$ (nickel bis(acetylacetonate))–Dibah (diisobutylaluminum hydride) catalyst system were performed on 10-methyl-1(9),7-hexalin-2-one[4,5] (1), and 1(9),7-hexalin-2-one[6] (2). For purposes of comparison, copper-catalyzed conjugate addition of alkyl groups was carried out[4,5] (see reactions 1–6). The structure of adduct 3 was assigned based on ^1H NMR and IR data and on literature precedent.[5] The structure of 5 was assigned by catalytic hydrogenation[7] of the side chain followed by GC and spectral comparison with 3. Compound 7 was assigned the same stereochemistry (at C-6) as 5, based on comparison of ^1H NMR spectral data.

Reactions using compound 2 were more complex. Copper-catalyzed conjugate addition yielded both cis and trans stereoisomers at C-6 in contrast to a published report.[6] Assignments of the cis and trans products 9 and 10 are not absolute since no comparison compound could be obtained, but structures were assigned by comparison of ^1H NMR data for the ring protons in 9 and 10 with that for ring protons in 3. (It has been shown that similar ring substitution patterns result in similar ^1H NMR spectra for these ring protons.[8]) Using the same strategy outlined in reactions 2 and 3, structures for the 1,6 adducts were assigned. Spectral comparison and GC coinjection of hydrogenated products supported these assignments. The 1,4 products 11 and 14 could not be completely characterized because of purification problems; structures were assigned primarily on the basis of IR spectra and mass spectral data. Highlighting the general elucidation of these addition reactions was the intriguing observation that the distribution of adducts formed by the cuprate procedures was *nearly identical* with that found for the nickel-catalyzed reaction of the alkenylzirconium complexes.



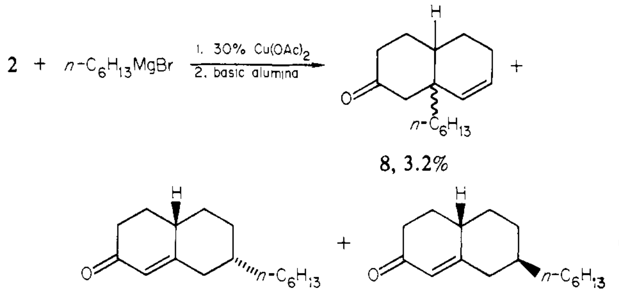
3, 20%



A, R = n-C_4H_9, 4
B, R = t-C_4H_9, 6

A, R = n-C_4H_9, 5 62%
B, R = t-C_4H_9, 7 77%

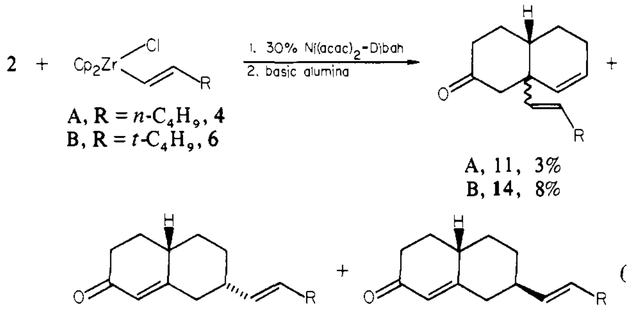
$$5 \xrightarrow{H_2/RhCl(PPh_3)_3} 3 \qquad (3)$$



8, 3.2%

9, 25%

10, 18%



A, R = n-C_4H_9, 4
B, R = t-C_4H_9, 6

A, 11, 3%
B, 14, 8%

A, 12, 27%
B, 15, 13%

A, 13, 19%
B, 16, 15%

$$12 \xrightarrow{H_2/RhCl(PPh_3)_3} 9$$
$$13 \xrightarrow{H_2/RhCl(PPh_3)_3} 10 \qquad (6)$$

Three pathways are a priori possible to explain the observed nickel-catalyzed additions: (1) (two-electron) nucleophilic attack, (2) double-bond insertion, and (3) an initial one-electron transfer to the enone. A (two-electron) nucleophilic attack pathway is analogous to a classical Michael reaction, and a double-bond

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(1) (a) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. (b) Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1978**, 4381. (c) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333.

(2) Schwartz, J.; Carr, D. B.; Hansen, R. T.; Dayrit, F. M. *J. Org. Chem.* **1980**, *45*, 3053.

(3) Corey, E. J. *J. Am. Chem. Soc.* **1955**, *77*, 1044.

(4) Marshall, J. A.; Ruden, R. A.; Hirsch, L. K. *Tetrahedron Lett.* **1971**, 759.

(5) Marshall, J. A.; Roebke, H. *J. Org. Chem.* **1966**, *31*, 3109.

(6) Birch, A. J.; Smith, M. *Proc. Chem. Soc.* **1962**, 356.

(7) Djerassi, C.; Gutzwiller, J. *J. Am. Chem. Soc.* **1966**, *88*, 4538.

(8) Jackman, L. M.; Sternhill, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 237.

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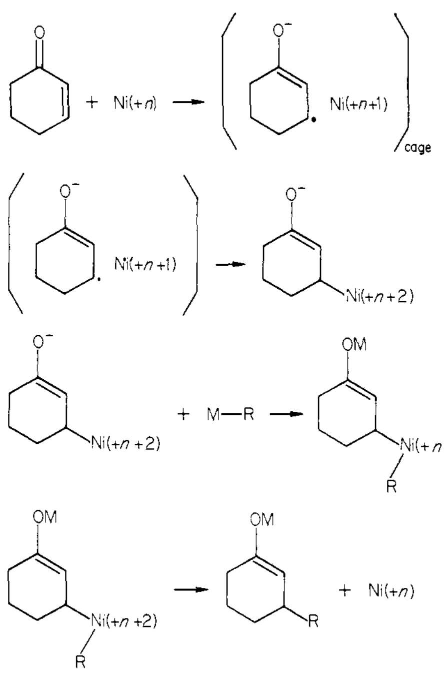
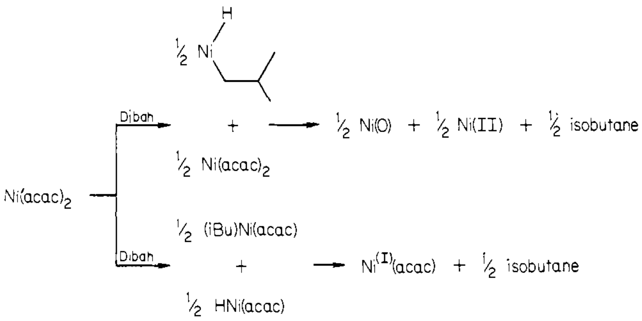
Scheme I. One-Electron-Transfer Mechanism



insertion pathway is similar to the mechanism proposed for nickel-catalyzed oligomerization of olefins.[9] An electron-transfer mechanism[10,11] is depicted in Scheme I. House[11] has argued in favor of electron transfer in copper-promoted conjugate addition reactions and has provided evidence for the existence of radical anions derived from one-electron reduction of enones.[11e,12] However, it could not be proven whether these radical anions were intermediates leading to product formation or whether they were formed in side reactions. He has also demonstrated a correlation between the success of copper-mediated conjugate addition reactions and the first electrochemical reduction potential of the enone substrate.[11a,c–e] No such correlation exists for nucleophilic additions to enones. Thus substrates with reduction potentials more negative than −2.4 V (vs. SCE) failed to react with "lithium dimethylcuprate", while those with potentials less negative than this value reacted successfully.[11a,e] Unfortunately, attempts to provide direct support for this electron-transfer mechanism were frustrated by failures to obtain an electrochemical oxidation wave from the cuprate reagent,[13] and controversy still exists concerning the mechanism of these reactions.[14]

As noted above, a similarity exists between the nickel- and copper-mediated conjugate addition reactions, for example, in that both give the same product distribution for conjugate additions to dienones **1** and **2**. However, *if* conjugate addition involving these two *apparently* different types of reagent systems proceeded by *comparable* mechanisms, then comparable selectivity might be expected. For example, if both reactions proceeded by an electron-transfer pathway, selectivity for coupling of the resulting ketyl would dictate the product distribution. To elucidate the nature of the nickel catalyst and to determine its mode of operation assumed a role of major significance.

Scheme II[a]



[a] No specific ligation other than that shown is implied.

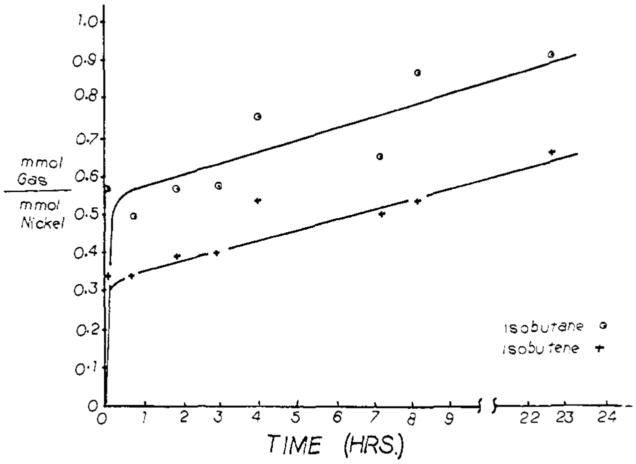


Figure 1. Gas evolution study: $Ni(acac)_2$ + Dibah → isobutane + isobutene.

Mechanistic Studies of Nickel-Catalyzed Conjugate Addition Reactions. A. Historical Development of the Nickel Catalyst. In our early studies[1a] of nickel-catalyzed conjugate addition reactions of alkenylzirconium compounds to α,β-enones, $Ni(acac)_2$ alone was used. In all of these $Ni(acac)_2$-based procedures some symmetrical diene was observed, resulting from coupling of two alkenyl units derived from the alkenylzirconium starting material. In fact, when the reaction between cyclohexenone, $Ni(acac)_2$, and **6** was monitored as a function of time, it was found that diene formation, although relatively slow, was always observed prior to the onset of conjugate addition.[15] Furthermore, it was noted that the solution formed by allowing $Ni(acac)_2$ to react with a small amount of an alkenylzirconium species (to give symmetrical diene) contained a highly active catalyst for conjugate addition of more alkenylzirconium reagent to subsequently added enone. The active form of the catalyst was thus postulated to be a reduced valent nickel species generated (slowly) by transfer of alkenyl groups from zirconium to Ni(II), followed by reductive elimination of diene. To avoid wasting potentially valuable alkenylzirconium starting material in the catalyst activation step, other activation means were studied, and it was found that reduction of $Ni(acac)_2$ (prior to reaction with enone and the alkenylzirconium) could be accomplished by addition of 1 equiv of Dibah. The active conjugate addition catalyst system thus obtained resulted in formation of essentially no dienic byproduct and remained active for conjugate addition reactions for several hours at 0 °C.

B. Gas Evolution Studies of the Reaction between $Ni(acac)_2$ and Dibah (1:1). Wilke and co-workers[16] reported that organoaluminum reagents reduced $Ni(acac)_2$ to Ni(0) with concomitant evolution of alkane and alkene (Scheme II). It is important to note that the stoichiometry for this reduction is *one* alkane formed

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[9] (a) Heimbach, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, *8*, 29. (b) Semmelhack, M. F. In "Organic Reactions"; Wiley: New York, 1972; Vol. 19, p 115.

[10] Posner, G. H. In "Organic Reactions"; Wiley: New York, 1972; ref 96, p 1.

[11] (a) House, H. O. "Organocopper Reagents in Organic Synthesis". Talk given at the R. A. Welch Foundation Conferences on Chemical Research, XVII, Houston, Texas, Nov 1973. (b) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 3128. (c) House, H. O.; Umen, M. J. *Ibid.* **1972**, *94*, 5495. (d) House, H. O.; Huber, L. E.; Umen, M. J. *Ibid.* **1972**, *94*, 8471. (e) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.

[12] House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2770.

[13] House, H. O.; Chu, C. Y. *J. Org. Chem.* **1976**, *41*, 3083.

[14] Casey, C. P.; Cesa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236.

[15] Carr, D. B. Ph.D. Dissertation, Princeton University, Princeton, N.J., 1978.

[16] Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 943.

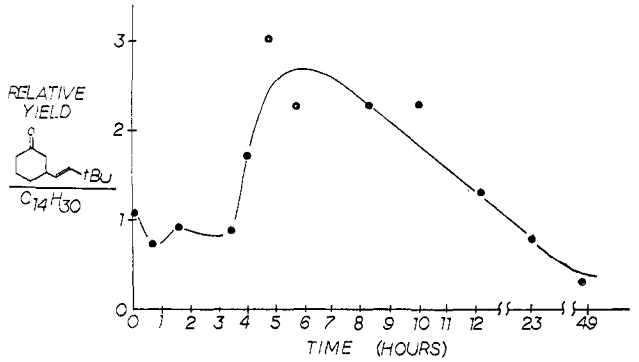

Figure 2. Ni(acac)$_2$–Dibah catalyst activity vs. catalyst digestion time monitored over 2 days.

per *unit* of Ni(II) reduced to Ni(0).

A study of the gases evolved in the reaction between an *equimolar* amount of Ni(acac)$_2$ and Dibah (in THF at 0 °C) was performed. The yield (over a period of 22 h) of gases was followed by gas chromatography (see Figure 1). The instantaneous production of 0.5 equiv of isobutane means that, under these conditions, initial reduction of Ni(II) to a (bulk) oxidation state of +1 is fast. Two possible explanations for this observation are: (case I) the solution contains an equimolar amount of Ni(II) and Ni(0), giving an average "oxidation state" of +1; or (case II), the solution contains actual Ni(I) species (vide infra). After this initial burst of gas, further reduction occurs slowly over the next 23 h, at which time 0.9 equiv of isobutane had been released, indicating that reduction to Ni(0) was almost complete. Previous studies on Ni–Al systems had involved Al:Ni $\geq$ 2; Ni(0) was always postulated to be formed from Ni(II) directly without the intermediacy of Ni(I) species. Nickel(I) species are known, however, under certain circumstances.[17,18] These have involved the use of weak reducing agents or hindered or basic phosphines. Apart from the observation[17,18] that the behavior of nickel species at Al:Ni = 1:1 vs. Al:Ni = 2:1 is different, little data exist in the literature concerning these systems.

Ni(acac)$_2$–Dibah Catalyst Activity. Having noted the gas evolution profile for Ni(acac)$_2$–Dibah, the activity of this system as a catalyst for conjugate addition was followed as a function of catalyst age. The Ni–Al catalyst system was prepared in one flask while in another the substrate (2-cyclohexenone), the zirconium reagent (**6**), and tetradecane (internal standard) were mixed together. At various time intervals an aliquot from each flask was withdrawn and allowed to react together in a separate flask for exactly 15 min. Control aliquots from the second flask were also taken. As can be seen from Figure 2, a complex situation exists: apparently at least two catalyst species are present and are distinguishable by their activities and lifetimes. An important observation is, however, that catalytic activity falls to an insignificant value concomitant with reduction of Ni to Ni(0). Maximum catalytic activity is associated with species believed, by the gas evolution studies noted above, to be described by either case I or case II (vide supra).

Electrochemical Studies. A mechanism involving a catalyst acting as an electron-transfer reagent implies that the catalyst can be readily oxidized. Electrochemical analysis (by cyclic voltammetry, CV) of species obtained by reaction between Ni(acac)$_2$ and Dibah (1:1) was therefore carried out. In this way these species could be characterized by their redox potentials and by their catalytic activity. As can be seen in the following cyclic voltammograms, these species are not electrochemically reversible. More than one anodic wave is associated with a single cathodic wave. The potentials[19] obtained in these experiments are quoted as E_{pa} or E_{pc}. The subscript "pa" signifies that the potential is measured at maximum wave height and that it is an anodic wave; E_{pc} refers to the cathodic wave. Since these are nonreversible potentials, this notation serves to distinguish it from potentials obtained for reversible systems.

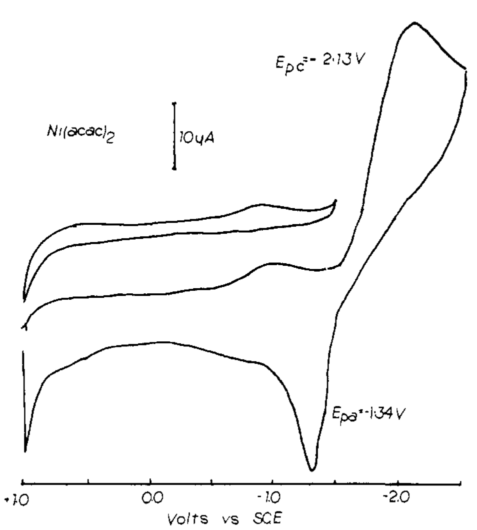

Figure 3. Ni(acac)$_2$: 1.0 mM in THF, 0.5 M n-Bu$_4$NClO$_4$, 23 °C; scan rate, 200 mV/s.

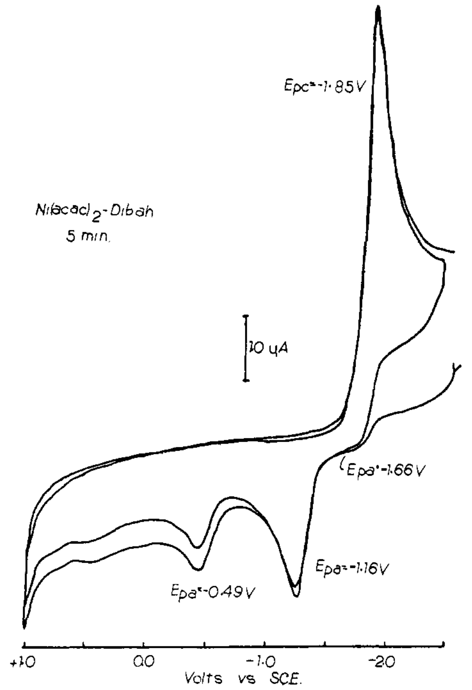

Figure 4. Ni(acac)$_2$–Dibah, 5 min after reduction: 1.3 mM in THF, 0.45 M n-Bu$_4$NClO$_4$, 23 °C; scan rate, 200 mV/s. Same conditions were used for CV's shown in Figures 5 and 6.

Ni(acac)$_2$. The CV of Ni(acac)$_2$ in THF is presented in Figure 3 (E_{pa} = −1.34 V, E_{pc} = −2.13 V; unless otherwise noted, potentials are measured vs. SCE). Ni(acac)$_2$ is, obviously, a complex of Ni(II). In order to assign the electrochemical redox transition, a wave-clipping experiment was performed. By scanning only over the position of the anodic wave (−1.5 to +1.0 V), no anodic current

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(17) (a) van Ommen, J. G.; Mars, P.; Gellinge, P. J. *J. Mol. Catal.* **1979**, *6*, 145. (b) van den Enk, J. E.; van der Ploeg, H. J. *J. Polymn. Sci., A-1* **1971**, *9*, 2395, 2403. (c) Shmidt, F. K.; Saraev, V. V.; Larin, G. M.; Lipovich, V. G.; Mironova, L. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, *9*, 2136. (d) Tkac, A.; Stasko, A. *Collect. Czech. Chem. Commun.* **1972**, *37*, 1006. (e) Holah, D. G.; Hughes, A. H.; Hui, B. C.; Wright, K. *Can. J. Chem.* **1974**, *52*, 299. (f) Areste, M.; Nobile, C. F.; Saco, A. *Inorg. Chim. Acta* **1975**, *12*, 167.

(18) van Ommen, J. G.; van der Ploeg, H. J.; van Berkel, P. C. J. M.; Mars, P. *J. Mol. Catal.* **1977**, *2*, 409.

(19) In a previous communication (Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102* 3976) we had quoted the positions of the redox potentials at wave half-height, $E_{1/2}$. Because of ambiguities involved in measurement and in order to follow convention, we quote the positions of the electrochemical waves as E_{pa} and E_{pc}.

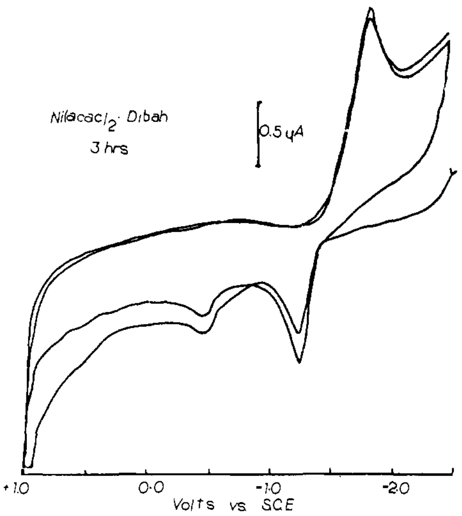


Figure 5. Ni(acac)$_2$–Dibah, 3 h after reduction.

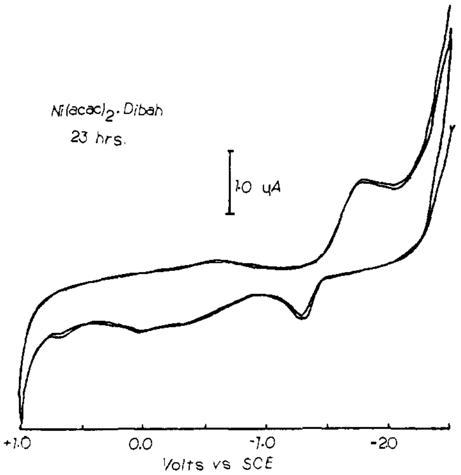


Figure 6. Ni(acac)$_2$–Dibah, 23 h after reduction.

was obtained. Therefore, prior reduction must occur before any oxidation species is detected. Dessy and co-workers[20] have determined the reduction potential of Ni(acac)$_2$ to be -2.2 V (vs. 1 mM $AgClO_4$/Ag reference, 0.1 M Bu_4NClO_4 electrolyte, dimethoxyethane, 22 °C). No corresponding oxidation current was observed under his conditions. Exhaustive controlled potential electrolysis showed that Ni(acac)$_2$ accepts one electron per molecule.[20] Based on this study[20] and based on the wave-clipping experiment described earlier, the reduction wave at $E_{pc} = -2.13$ V is assigned as Ni(II) → Ni(I), while the oxidation wave at $E_{pa} = -1.34$ is assigned as Ni(I) → Ni(II).

Ni(acac)$_2$–Dibah. The CV's of Ni(acac)$_2$ + Dibah taken at three time intervals are shown in Figures 4–6. The first and most interesting aspect to note is the presence of at least three distinct anodic waves (E_{pa} = -1.66, -1.16, and -0.49 V) one large cathodic wave (E_{pc} = -1.85 V); each of the voltammograms records the first two scans.

The relationship between these peaks was probed by wave-clipping experiments. Scanning from -2.5 to -1.0 V, Figure 7A is obtained containing two anodic waves and one cathodic wave. As shown in Figure 7B, limiting the scan from -2.5 to -1.5 V reveals that the anodic wave at -1.66 V is unchanged but that the cathodic wave is greatly diminished in size. This is consistent with a situation where two anodic waves correspond to separate species which, upon oxidation, give a common intermediate. Such species may be, for example, clusters consisting of different numbers of Ni-containing subunits which, on oxidation, may become labilized (see Scheme III).

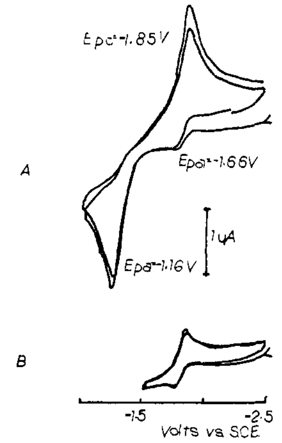


Figure 7. Ni(acac)$_2$–Dibah, 15 min after reduction, 1.0 mM in THF, 0.5 M n-Bu_4NClO_4, 0 °C; scan rate, 200 mV/s.

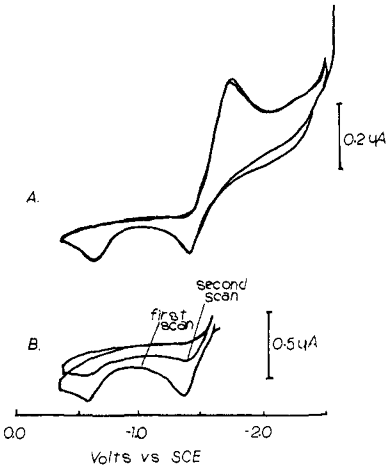
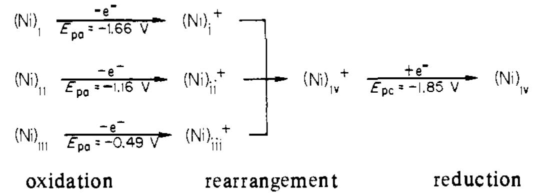


Figure 8. Ni(acac)$_2$–Dibah, ca. 30 min after reduction, 1.3 mM in THF, 0.45 M n-Bu_4NClO_4, 23 °C; scan rate, 200 mV/s.

Scheme III



The species due to E_{pa} = -1.66 and -0.49 V have only transient existence. The former disappears after about 20 min while the latter is nearly gone after about 3 h at room temperature. This supports the contention that the three species exist independently.

The CV taken after 30 min at 23 °C is shown in Figure 8, in which the scan is limited from -2.5 to -0.25 V. As shown in Figure 8B, on further limiting the range from -1.5 to -0.25 V, an anodic wave is obtained on the first scan, but by preventing subsequent electrochemical reduction, the anodic wave disappears on succeeding scans. This suggests that the species due to the anodic wave may be initially present in solution and are not generated electrochemically. It also shows that the anodic waves at E_{pa} = -1.16 and -0.49 V are coupled to the cathodic wave at E_{pc} = -1.85 V. In summary then:

(1) At least three independent oxidizable species are present in solution. These are distinguishable by their redox potentials. CV readings at 5 min, 3 h, and 23 h show that these species have different lifetimes. After about 20 min at 23 °C the species at -1.66 V disappears; after about 3–4 h at 23 °C the -0.49 V wave is gone; at 23 h only the -1.16 V wave is present although in greatly diminished size.

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[20] Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.

Scheme IV

$$\mathrm{L_2Ni^{I}X + ArX \longrightarrow L_nNi^{III}ArX_2}$$

$$\mathrm{L_nNi^{III}ArX_2 + M\text{-}R \longrightarrow L_nNi^{III}Ar(R)X + M\text{-}X}$$

$$\mathrm{L_nNi^{III}Ar(R)X \longrightarrow L_nNi^{I}X + Ar\text{-}R}$$

(2) All three oxidation waves are coupled to the same reduction wave, indicating a common intermediate for the three species.

(3) Wave-clipping studies suggest that the species originally present in solution is the reduced species.

By comparison with the CV obtained for $Ni(acac)_2$, the −1.16-V anodic wave is assigned a Ni(I) → Ni(II) transition. However, since all three anodic waves appear to give rise to the same intermediate, they must all have the same oxidation state (as, for example, is shown in Scheme III).

These electrochemical data are consistent with the gas evolution results that suggest the presence of a Ni(I) species (case 2). These results also are consistent with the catalyst activity vs. time profile described above. In other words, there exists a correlation between oxidation potentials measured for the catalyst system by CV and its chemical action. Based on this concept it was predicted that $Ni(PPh_3)_4$ (E_{pa} = −0.34 V, THF) would be inactive toward catalysis of conjugate addition, and it was found to be so.

Chemical Correlations. To substantiate the contention that $Ni(acac)_2$–Dibah is a reducing agent, several experiments were performed in which it was known that reducing ability would correlate with the success of a chemical transformation.

A. **Reaction with *p*-Benzoquinone.** *p*-Benzoquinone is a moderately strong oxidizing agent that undergoes stepwise reduction by successive one-electron transfers.[21] Under aprotic conditions it exhibits two redox couples at $E_{1/2}$ = −0.49 and −1.28 V (vs. SCE, THF, 0.5 M n-Bu_4NClO_4).

Kochi[21a] has investigated the possibility of electron transfer from zerovalent nickel(phosphine) complexes to organic electron acceptors such as tetracyanoethylene, chloranil, and dichlorodicyanobenzoquinone. He concluded that electron transfer from Ni(0) to potent oxidizing agents such as these is feasible.

Hegedus proposed a similar electron-transfer scheme in the reaction between (π-allylic)nickel(II) species and alkyl-substituted *p*-benzoquinones.[22] By comparison of the reaction products with spin density of the quinone radical anion as determined by ESR, it was found that coupling occurred at the position of highest spin density. Furthermore, a correlation was shown between the first reduction potential of these benzoquinones and the success of the coupling reaction: substrates with reduction potentials less negative than $E_{1/2}$ = −0.88 V (vs. SCE in DMF) were successful. As measured by CV, the $Ni(acac)_2$–Dibah system gives rise to readily oxidizable Ni(I) species which should be more potent electron-transfer reagents than Ni(II) analogues. Indeed, reaction between $Ni(acac)_2$–Dibah (1:1) and *p*-benzoquinone gave hydroquinone upon hydrolysis. Conjugate addition to *p*-benzoquinone, however, failed using **6** and this reagent mixture. This failure may be due to, for example: (1) over-reduction of benzoquinone directly to hydroquinone dianion may have occurred, making coupling impossible, or (2) the Ni(II) species that is produced after the initial electron transfer may not be an efficient trap for the (somewhat stable) benzoquinone radical anion. (The π-allylnickel(II) bromide used by Hegedus[22] may be a less powerful electron donor; the oxidized product may also be a better radical trap.)

B. **$Ni(acac)_2$–Dibah (1:1)-Catalyzed Coupling of Aryl Halides and Alkenylzirconium Reagents.** Negishi and co-workers[23,24] have developed procedures for the cross-coupling of aryl halides with alkenylaluminum or -zirconium reagents using a $Ni(acac)_2$–Dibah–$4PPh_3$ catalyst system (Ni–Al–P). These reactions likely involve activation of the aryl halide by oxidative addition to a low-valent nickel species (reaction 7). Kochi[25,26] has described the mechanism of oxidative addition of aryl halides to Ni(0) complexes as proceeding through a rate-determining electron-transfer step. He has also proposed[27] that Ni(I) species are involved as the catalytically active species in Ni-*catalyzed* coupling reactions of aryl halides (Scheme IV). It is likely that here, too, an electron-transfer step is critical to the activation of the aryl halide. In such a scheme, then, the ability of a catalyst species to add an electron to the aryl halide substrate would determine the outcome of the catalytic cycle (assuming that transmetalation and reductive elimination were feasible, of course). To examine the ability of $Ni(acac)_2$–Dibah (1:1) (Ni–Al) as a catalyst in coupling reactions was therefore of interest, and a brief study of this procedure was carried out.

Table I

entry	phenyl halide	catalyst[a]	conditions (temp/h)	% yield (VPC) coupled product
1	I	Ni-Al-P	amb/12	quant
2	Br	Ni-Al-P	amb/12	quant
3	Br	Ni-Al	0/3.5	67[b]
4	Br	Ni-Al-P	0/3.5	0
5	Cl	Ni-Al	0/3.5	6.2
6	Cl	Ni-Al-P	0/3.5	0
7	I	$NiCl(PPh_3)_3$	0/3.5	35.7
8	I	$NiCl(PPh_3)_3$	amb/20	79.6
9	Br	$NiCl(PPh_3)_3$	0/3.5	1.7
10	Br	$NiCl(PPh_3)_3$	amb/20	28.3
11	Cl	$NiCl(PPh_3)_3$	0/3.5	0.95
12	Cl	$NiCl(PPh_3)_3$	amb/20	8.7
13	Br	$Ni(PPh_3)_4$	0/3.5	1.8
14	Br	$Ni(PPh_3)_4$	amb/20	40.0

[a] Catalyst = 0.1–0.2 equiv added based on aryl halide. [b] Isolated yield.

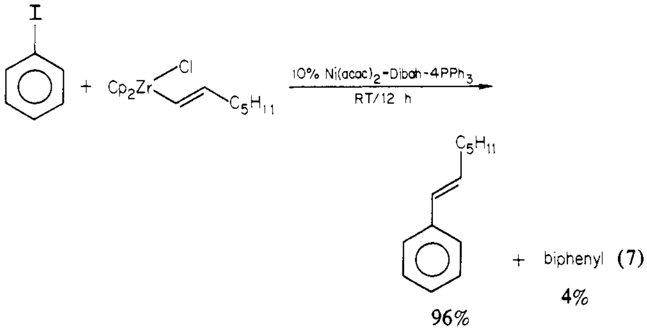
Scheme V

$$\mathrm{[Ni^{I}] + ArX \longrightarrow [Ni^{II}ArX^{-}\cdot]}$$

$$\mathrm{[\dot{N}i^{II}ArX^{-}\cdot] \longrightarrow [Ni^{III}(Ar)X]}$$

$$\mathrm{[Ni^{III}(Ar)X] + (Zr)\text{-}R \longrightarrow [Ni^{III}Ar(R)] + (Zr)\text{-}X}$$

$$\mathrm{[Ni^{III}Ar(R)] \longrightarrow [Ni^{I}] + ArR}$$



For the sake of comparison, analogous reactions under identical conditions were performed using Ni–Al, Ni–Al–P, $Ni(PPh_3)_4$, and $NiCl(PPh_3)_3$ as catalyst species. It was of specific interest to determine if reactivity of these catalyst systems would correlate with their oxidation potentials as measured by CV. Two of the reactions of the Ni–Al–P system were performed under conditions described in the literature (23 °C, 12 h).[23,24] Results are summarized in Table I. These data provide a sharp contrast between the reactivity of these systems. Entries 3, 4, 9, and 13 highlight this demarcation. These results are consistent with CV deter-

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minations, and they support the notion that an initial electron transfer is the rate-determining step in a proposed mechanism analogous to the one described by Kochi.[25,26] However, in this case the nickel catalyst is *already* in a Ni(I) ↔ Ni(III) redox manifold and does not have to be activated (Scheme V).

Conclusions

On the basis of our determinations that the $Ni(acac)_2$–Dibah (1:1) system gives rise to transient species which are good reducing agents, whose lifetimes correlate with conjugate addition and whose oxidation potentials correlate both with conjugate addition and with aryl–alkenyl coupling, we propose that the conjugate addition reaction proceeds by an initial electron-transfer pathway as shown in Scheme I, in which the various reduced Ni species present in the reaction mixture each can serve as "Ni(I)", each with a different efficiency for the overall process. We have recently isolated material which electrochemically corresponds to the longest lived catalytically active species ($E_{pa} = -1.66$ V). We are attempting to characterize this species structurally so that additional details concerning the nature of conjugate addition can be obtained.

Experimental Section

General. All experiments were performed under an atmosphere of nitrogen unless indicated. High-purity-grade nitrogen was passed through a bed of BTS catalyst (previously reduced by heating under a CO stream) and a column of Matheson size 4A molecular sieves. Solid transfers were performed with a stream of N_2 or in a drybox (Vacuum Atmospheres Co.). All hydrocarbon or ethereal solvents were freshly distilled under an N_2 atmosphere from sodium/benzophenone ketyl with ca. 5% tetraglyme added to ensure solubility of ketyl. Other solvents were distilled under N_2 atmosphere from the proper drying agent. Commercially obtained organic compounds were dried by the appropriate method, and, if liquid, distilled under an N_2 atmosphere.

Analytical vapor phase chromatography (VPC) was carried out using the following: (A) $^1/_4$ in. × 8 ft aluminum 5% Carbowax 20M on Chromosorb P NAW 60/80, (B) $^1/_4$ in. × 8 ft aluminum 5% DEGS on Chromosorb P NAW 80/100, (C) $^1/_4$ in. × 20 ft aluminum 10% Carbowax 20M on Chromosorb P NAW 60/80, (D) $^1/_4$ in. × 6 ft aluminum 5% OV 210 on Chromosorb P NAW 60/80, (E) $^1/_8$ in. × 6 ft glass 3% Carbowax 20M on Chromosorb P NAW 60/80, (F) $^1/_8$ in. × 6 ft glass 3% DEGS on Chromosorb P NAW 60/80, (G) $^1/_8$ in. × 2 ft glass 3% OV 210 on Chromosorb P NAW 60/80, (H) $^1/_4$ in. × 6 ft glass 20% QF-1.

Nickel bis(acetylacetonate) [$Ni(acac)_2$] was purified by extraction with ether followed by sublimation at 130–140 °C in vacuo. $Ni(acac)_2$ was stored in the drybox. Diisobutylaluminum hydride (Dibah), obtained from Texas Alkyls, Inc., as a neat liquid, was diluted as indicated with dry benzene or hexane.

Preparation of Alkenylzirconocene Chlorides 4 and 6. Alkenylzirconocene chlorides, (*E*)-3,3-dimethyl-1-butenyl- (**6**) and (*E*)-1-hexenyl- (**4**), were prepared according to the procedures developed by Hart.[28b]

Nickel-Catalyzed Conjugate Addition to Enones Using Alkenylzirconocene Chloride Reagents. The following is a general procedure for the conjugate addition of alkenyl groups from alkenylzirconocene chloride reagents to α,β-enones. Various catalysts were used. Specific procedures using these catalysts are described below. The catalyst (15–20% molar equiv) is dissolved in 10 mL of THF at 0 °C. The substrate (1 equiv), zirconocene reagent (1.3 equiv), and internal standard (optional) are dissolved in 10 mL of THF and added dropwise at 0 °C over 15 min. The reaction mixture is stirred for 3–3.5 h, hydrolyzed with saturated aqueous NH_4Cl, washed with $NaHCO_3$ and brine, dried over Na_2SO_4, concentrated on the rotary evaporator, and distilled in vacuo or purified by liquid chromatography.

Following are the procedures used for the two catalysts.

(1) **$Ni(acac)_2$–Dibah.** Nickel bis(acetylacetonate) is dissolved in THF, cooled to 0 °C, and reduced with an equimolar amount of Dibah at 0 °C. The enone and zirconium reagent mixture are immediately added.

(2) **$Ni(acac)_2$–Dibah–4PPh_3.** Nickel bis(acetylacetonate) and 4 equiv of PPh_3 are dissolved in THF, cooled to 0 °C and reduced with an equimolar amount of Dibah at 0 °C. The enone and zirconium reagent mixture are immediately added.

(3) **$Ni(acac)_2$–Alkenylzirconocene Chloride.** An equimolar amount of $Ni(acac)_2$ and alkenylzirconocene chloride are dissolved in THF and stirred until the reaction becomes dark. For compounds **6** and **4** reduction is observed within 5 min at room temperature.

(4) **$NiCl(PPh_3)_3$ and $NiCl_2(PPh_3)_2$.** These compounds are dissolved in THF at 0 °C and the enone and zirconium reagent mixtures are added.

Tris(triphenylphosphine)nickel Chloride. The title compound was prepared according to the method of D'Aniello and Barefield[31] by synproportionation of $Ni(PPh_3)_4$ and $NiCl_2(PPh_3)_2$. Tetrakis(triphenylphosphine)nickel was prepared following Schunn's procedure.[32]

Bis(triphenylphosphine)nickel Dichloride[33] was prepared as follows. Nickel dichloride hexahydrate (4.76 g, 0.02 mol) in water (4 mL) was diluted into glacial acetic acid (100 mL). Triphenylphosphine (10.50 g, 0.04 mol) in 50 mL of glacial AcOH was added. The solution was stirred for 2 days at room temperature. The olive-green solution was filtered, yielding dark blue crystals which were washed with more glacial AcOH. It was dried in vacuo in the presence of KOH for 1 day and at 130 °C for another day, giving dry $NiCl_2(PPh_3)_2$. $Ni(PPh_3)_4$ (1.14 g, 1.03 mmol), $NiCl_2(PPh_3)_2$ (0.61 g, 1.03 mmol), and PPh_3 (0.22 g, 1.03 mmol) were suspended in 50 mL of benzene. The reddish color was discharged after ca. 20 s, giving a pale yellow solution. The reaction was heated to 58 °C for 10 min, then cooled to room temperature. Upon cooling in an ice bath, bright yellow precipitate, $NiCl(PPh_3)_3$, was obtained. It was filtered in the drybox, washed with 50 mL of ether, and dried in vacuo overnight.

Activity of $Ni(acac)_2$–Dibah Catalyst for Conjugate Addition vs. Catalyst Digestion Time. Into a 50-mL Schlenk flask "A" was weighed $Ni(acac)_2$ (0.052 g, 0.20 mmol). It was dissolved in 16 mL of THF and cooled to 0 °C. Into a 250-mL Schlenk flask "B" was weighed 2-cyclohexenone (0.5985 g, 6.2 mmol), **6** (3.47 g, 10.2 mmol), and tetradecane (0.1579 g) as internal standard. These were dissolved in 128 mL of THF and cooled to 0 °C. At time = 0, the $Ni(acac)_2$ was reduced with Dibah (0.27 mL, 0.75 M). At various time intervals thereafter, a 2-mL aliquot from flask A and 16 mL from flask B were withdrawn via syringe and allowed to react in a third flask under N_2 at 0 °C for exactly 15 min. Each reaction mixture was worked up in an identical fashion as follows: hydrolyzed with saturated aqueous NH_4Cl, washed with $NaHCO_3$ and brine, concentrated on the rotary evaporator, evaporatively distilled, and then analyzed by VPC on column B.

Preparation of 10-Methyl-1(9),7-hexalin-2-one (1). The procedure for the preparation of **1** was taken from the method of Heathcock and Ellis[29] and Angello and Laubach.[30] The product gave satisfactory spectral data (^{1}H NMR, IR, MS) and GC purity.

Copper-Catalyzed 1,6-Conjugate Addition of an *n*-Hexyl Group to 1. This procedure follows closely from Marshall and Roebke.[5] *n*-Hexyl Grignard was prepared via the standard route using freshly distilled 1-bromohexane (4.635 g, 28.1 mmol) and magnesium turnings (0.713 g, 29.3 mmol). In a separate dry 100-mL Schlenk flask were dissolved $Cu(OAc)_2$ (0.507 g, 2.5 mmol) and **1** (1.345 g, 8.3 mmol) in 50 mL of THF. The flask was cooled to −22 °C; then the previously prepared Grignard solution was added dropwise over 30 min via cannula, taking care to prevent addition of solid residue. The reaction temperature was maintained at −20 to −10 °C throughout the addition, after which it was allowed to warm to room temperature over 2 h, then refluxed for 15 min. It was hydrolyzed by pouring into saturated aqueous NH_4Cl, extracted with 3 × 70 mL Et_2O, washed with 2 × 100 mL brine, dried over Na_2SO_4, concentrated on the rotary evaporator, and then eluted through a column of basic alumina (Brockmann activity 1). The resulting mixture was purified by LC (20% EtOAc/hexane), giving the 1,6-adduct **3**, in 20.3% yield, 0.417 g: ^{1}H NMR (CCl_4) δ 5.45 (d, 1, J = 1.5 Hz), 2.45–1.35 (m, 10), 1.20 (br m, 14), 0.84 (s, 3); ^{13}C NMR ($CDCl_3$) δ 198.258, 168.665, 125.503, 37.718, 36.934, 35.760, 35.592, 34.418, 33.778, 31.507, 31.047, 29.033, 27.022, 25.212, 22.299, 22.098, 13.754; IR (neat) =C(H) 3015 cm^{-1}, C=O 1674 cm^{-1}; mass spectrum (m/e) 248 (97.8), 220 (45.7), 206 (38.0), 163 (100), 121 (59.8).

$Ni(acac)_2$-Dibah-Catalyzed 1,6-Conjugate Addition of an Alkenyl Group to 1. Nickel bis(acetylacetonate) (0.2034 g, 0.79 mmol) was weighed into a 100-mL Schlenk flask, dissolved in 10 mL of THF and cooled to 0 °C. Dibah (1.6 mL, 0.5 M) was syringed into the flask. From a dropping funnel were slowly added the dienone, **1** (0.8219 g, 5.07 mmol), and **4** (2.0121 g, 5.92 mmol) in 50 mL of THF. The reaction flask was allowed to warm to room temperature and was stirred for 5 h. It was hydrolyzed by pouring into aqueous 5% H_2SO_4, extracted with 3 × 30 mL of Et_2O, washed with 3 × 70 mL of $NaHCO_3$ and 2 × 70 mL of brine, dried over Na_2SO_4, and then concentrated by rotary evapora-

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tion. The reaction mixture was then eluted through a column of basic alumina (Brockmann activity 1) and purified by LC (20% EtOAc/hexane) giving **5**, 0.627 g (62%), and starting dienone **1**, 0.078 g (11.8%). Spectral data for **5** are as follows: ^{1}H NMR (CCl$_4$) δ 5.50 (d, 1, J = 1.5 Hz), 5.37 (t of d, 1, J = 3 and 16 Hz), 5.15 (d of d, 1, J = 2 and 16 Hz), 2.7–0.8 (m, 23); IR (neat) =C(H) 3023, C=O 1675 cm^{-1}; mass spectrum m/e 246 (100), 189 (50), 135 (28.6), 124 (64.3), 67 (40.0).

The double bond on the side chain was selectively hydrogenated according to the method of Djerassi and Gutzwiller.[7] Compound **5** (0.19 g, 0.78 mmol) and tris(triphenylphosphine)rhodium chloride (0.143 g, 0.16 mmol) were dissolved in 20 mL of ethanol and 20 mL of toluene in a Schlenk flask. After flushing the flask through with H$_2$ for 15 min, the reaction was allowed to stir under 1 atm of H$_2$ for 19.5 h. A total of 26.0 mL of H$_2$ was taken up. The solvent was evaporated and the residue extracted with 1:1 hexane/methylene chloride. Filtration through alumina, followed by LC purification, yielded pure **3** as verified by IR, ^{1}H NMR, ^{13}C NMR, and GC coinjection.

The same procedure was used to conjugatively add the (E)-3,3-dimethyl-1-butenyl group to **1** using the zirconium reagent **6**. Compound **7** was obtained in 76.5% yield. Compound **7** was further purified by preparative VPC on column A: ^{1}H NMR (CDCl$_3$) δ 7.29 (br s, 1), 5.51 (d, 1, J = 16 Hz), 5.25 (d of d, 1, J = 4.4 and 16 Hz), 2.71–2.02 (m, 11), 1.26 (s, 3), 0.96 (s, 9); ^{13}C NMR (CDCl$_3$) δ 199.19, 169.40, 142.42, 126.06, 125.95, 38.08, 37.22, 36.95, 36.08, 35.92, 34.13, 32.89, 30.74, 27.20, 22.37; IR (neat) =C(H) 3011, C=O 1670, t-Bu 1379, 1389 cm^{-1}; mass spectrum m/e 246 (58.3), 229 (12.9), 203 (43.2), 190 (74.6), 163 (72.1). Elemental analysis. Calcd: C, 82.86; H, 10.64. Found: C, 82.86; H, 10.33.

Preparation of 1(9),7-Hexalin-2-one (2). The procedure for the synthesis of **2** was taken from Birch and co-workers. The product gave satisfactory analysis by ^{1}H NMR, IR, MS, and VPC.

Copper-Catalyzed Conjugate Addition of an n-Hexyl Group to 1(9),7-Hexalin-2-one (2). The procedure is similar to that developed by Marshall and Roebke.[5] n-Hexyl Grignard was prepared in the standard fashion using freshly distilled 1-bromohexane (6.60 g, 40 mmol) and magnesium turnings (4.86 g, 0.2 mol) in ether. In a separate dry flask were dissolved Cu(OAc)$_2$ (0.7204 g, 3.6 mmol) and **2** (0.5589 g, 10.5 mmol) in 45 mL of THF. The flask was cooled to −20 °C and the Grignard solution was added dropwise over 30 min. The reaction mixture was then allowed to warm to room temperature over 2.5 h and then refluxed for 15 min. It was hydrolyzed by pouring into saturated aqueous NH$_4$Cl, washed with NaHCO$_3$ and brine, and dried over Na$_2$SO$_4$. The reaction mixture was eluted through a column of basic alumina (Brockmann activity 1), purified on a Waters Assoc. LC 500 (10% EtOAc/hexanes), then further isolated by preparative VPC. There was obtained 0.080 g of a compound tentatively assigned as **8** (3.2% yield): IR (neat) C=O 1714 cm^{-1}; mass spectrum m/e 234 (8.1), 206 (8.1), 151 (100), 133 (13.8), 121 (12.6). Compound **9** was obtained in 25% yield (0.529 g): ^{1}H NMR (CDCl$_3$) δ 5.82 (br s, 1), 2.80–0.70 (m, 24); IR (neat) C=O 1676 cm^{-1}; mass spectrum m/e 234. Compound **10** was isolated in 18% yield (0.452 g): ^{1}H NMR (CDCl$_3$) δ 5.68 (br s, 1), 2.45–0.70 (m, 24); IR (neat) C=O 1676 cm^{-1}; mass spectrum m/e 234 (93.3), 206 (68.7), 149 (100), 121 (86.6), 107 (59.0).

Nickel-Catalyzed Conjugate Addition of an Alkenyl Group to 1(9),7-Hexalin-2-one (2). Into a 100-mL Schlenk flask was weighed Ni(acac)$_2$ (0.771 g, 2.94 mmol) dissolved in 10 mL of THF and cooled to 0 °C. From a dropping funnel were added **2** (1.520 g, 10.3 mmol) and **4** (4.385 g, 12.9 mmol) dissolved in 70 mL of THF. The reaction was stirred at 0 °C for 2.5 h. It was hydrolyzed by pouring into 5% aqueous H$_2$SO$_4$ and extracted with 3 × 100 mL of ether, washed with saturated aqueous NaHCO$_3$ and brine, and dried over Na$_2$SO$_4$. The crude mixture was then eluted through basic alumina (Brockmann activity 1), purified on a Waters Assoc. LC 500 (10% EtOAc/hexanes), then by preparative VPC. Compound **11** was isolated in 3% yield (0.66 g): ^{1}H NMR (CDCl$_3$) δ 5.39 (m), 2.75–0.75 (m); IR (neat) =C(H) 3013, C=O 1714, (E)CH=CH 1668, (Z)CH=CH 1621 cm^{-1}. Compound **12** was isolated in 27% yield (0.644 g): ^{1}H NMR (CCl$_4$) δ 5.67 (br s, 1), 5.37 (m, 2), 2.70–0.85 (m); IR (neat) =C(H) 3013, C=O 1675, (E)CH=CH 1621 cm^{-1}; mass spectrum m/e 232 (100), 175 (70.1), 162 (25.3), 147 (39.0), 110 (46.1). Hydrogenation of **12** was carried out using Djerassi's method.[7] VPC coinjection of the hydrogenated product showed it to be identical with **9**. Compound **13** was obtained in 19% yield (0.456 g): ^{1}H NMR (CCl$_4$) δ 5.66 (br s, 1), 5.35 (m, 2), 2.8–0.75 (m); IR (neat) =C(H) 3014, C=O 1679, (E)CH=CH 1623 cm^{-1}; mass spectrum m/e 232 (100), 175 (70), 164 (36.0), 162 (30.3), 147 (52.8). Compound **13** was similarly hydrogenated, giving **10** as identified by GC coinjection, ^{1}H NMR, IR, and MS comparison. Starting material **2** was recovered in 15.6% yield (0.237 g). Similarly, the (E)-3,3-dimethyl-1-butenyl side chain was appended to **2** using the zirconium reagent **6**. Compound **14** was obtained in 8% yield: ^{1}H NMR (CDCl$_3$) δ 6.09 (d of d, 1, J = 3 and 8 Hz), 5.82 (d of d, 1, J = 3 and 5 Hz), 5.46 (d, 1, J = 16 Hz), 5.26 (d of d, 1, J = 5 and 16 Hz), 2.77–0.95 (m); mass spectrum m/e 232 (82.4), 217 (10.8), 189 (17.6), 175 (35.1), 149 (66.2), 148 (100), 147 (89.2). Exact mass analysis. Calcd: 232.1827. Found: 232.1829 ± 0.0007. Compound **15** was obtained in 12.8% yield: ^{1}H NMR (CDCl$_3$) δ 5.85 (br s, 1), 5.50 (d, 1, J = 16 Hz), 5.21 (d of d, 1, J = 4.5 and 16 Hz), 2.74–1.27 (m, 12), 0.96 (s, 9); ^{13}C NMR (CDCl$_3$) δ 199.91, 165.99, 142.58, 126.17, 126.01, 44.367, 39.925, 39.004, 37.867, 36.837, 36.621, 30.662, 29.741, 29.361; IR (neat) C=O 1671 cm^{-1}; mass spectrum m/e 232 (75.9), 217 (10.8), 189 (26.4), 176 (34.9), 162 (31.0), 149 (100), 148 (99.5), 147 (93.7). Exact mass analysis. Calcd: 232.1827. Found: 232.1829 ± 0.0007. Compound **16** was obtained in 15% yield: ^{1}H NMR (CDCl$_3$) δ 5.83 (br s, 1), 5.51 (d, 1, J = 16 Hz), 5.19 (d of d, 1, J = 5.4 and 16 Hz), 2.49–1.25 (m, 12), 0.99 (s, 9); ^{13}C NMR (CDCl$_3$) δ 199.914, 166.312, 140.688, 128.661, 124.598, 42.146, 41.767, 37.433, 36.566, 33.804, 32.720, 32.503, 29.741, 29.036; IR (neat) C=O 1678 cm^{-1}; mass spectrum m/e 232 (71.7), 217 (10.2), 189 (22.6), 175 (30.3), 162 (25.5), 149 (84.8). Exact mass analysis. Calcd: 232.1827. Found: 232.1829 ± 0.0007.

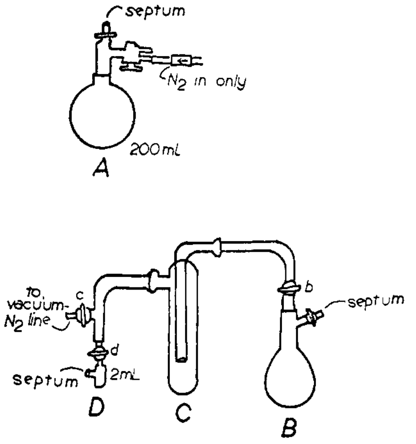

Figure 9. Apparatus for isobutane evolution studies.

Studies on the Ni(acac)$_2$-Derived Catalysts. A. Gas Evolution Study: Ni(acac)$_2$ + Dibah. The experimental setup is illustrated in Figure 9. The 200-mL round-bottomed flask A was fitted as shown with a septum and a two-way stopcock. One of the inlets was fitted with a one-way valve so that when left in this position, nitrogen could only flow into the flask. Into flask A was weighed Ni(acac)$_2$ (1.285 g, 5.01 mmol). The flask and vacuum line were purged of air and filled with N$_2$ for three cycles, after which the two-way stopcock was left in the "N$_2$ in only" position. The sampling apparatus was also purged of air and filled with N$_2$. n-Pentane (0.405 g) was introduced into flask A after which the flask was filled to the neck with ca. 200 mL of THF and cooled to 0 °C. At time = 0 the Ni(acac)$_2$ was reduced with Dibah (5.01 mL, 1.0 M). At various time intervals a 3-mL aliquot was syringed from flask A and transferred to flask B which was also cooled to 0 °C. The volatiles were evacuated into flask C by cooling C to −196 °C and pumping on the system. Then with stopcocks b and c shut and d open, flask C was warmed with a heat gun while cooling flask D to −196 °C to condense all the volatiles. After completion of transfer, flask D was warmed to −78 °C, then analyzed by VPC on column C.

B. Isolation of Black Crystals from Ni(acac)$_2$–Dibah. Ni(acac)$_2$ (2.57 g, 10 mmol) was weighed into a 100-mL Schlenk flask, dissolved in 40 mL of Et$_2$O, and cooled to 0 °C. It was reduced with Dibah (10 mL, 1.0 M) and then stirred for 3 h at 0 °C. The solvent was removed in vacuo and the residual solid was pumped on for 3 h at room temperature. The flask was cooled to −78 °C and 30 mL of pentane was introduced. The solution was stirred for 30 min and let stand for 2 h. It was filtered under an N$_2$ atmosphere through a glass frit. The black crystals were then washed with pentane and dried overnight in vacuo. They were stored in the drybox until further use.

C. Electrochemical Experiments. Electrochemical analyses were performed using a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a PAR 176 current-to-voltage converter. The cyclic voltammetry (CV) program was generated by a PAR Model 175 universal programmer. Voltammograms were recorded on a Hewlett-Packard 7041 A X-Y recorder. A Beckmann Instruments working electrode with a 5-mm diameter platinum button was used. A platinum wire served as the counter electrode. All potentials were referenced to a saturated calomel electrode (SCE). The SCE was placed in the arm which was filled with saturated aqueous KBr to provide electrical contact between the electrode and the tip of the arm. The tip of the arm consisted of a "thirsty glass" plug sealed in place with heat-shrinkable polyethylene. The tip was positioned as close to the working electrode as possible to minimize ohmic drop.

Tetra-*n*-butylammonium perchlorate (Eastman), the supporting electrolyte, was purified by recrystallization from ethyl acetate twice and drying in vacuo at 140 °C for 10 h. It was stored in the drybox. All cell preparations were done in the drybox and all electrochemical experiments were performed under N_2 atmosphere in quiet solutions. Typically, 70 mL of solvent and 10 g of n-Bu_4NClO_4 were used. Samples were 1 mM in concentration.

D. **Attempted Addition of an Alkenyl Group to *p*-Benzoquinone Catalyzed by Ni(acac)$_2$–Dibah.** Nickel bis(acetylacetonate) (0.0825 g, 0.32 mmol) was dissolved in 3 mL of THF, cooled to 0 °C, and reduced with Dibah (0.65 mL, 0.5 M). Via a dropping funnel were added sublimed *p*-benzoquinone (0.2307 g, 2.14 mmol) and **6** (1.1 g, 3.12 mmol) in 10 mL of THF. After 2 h at 0 °C the dark solution turned yellowish. At 4 h the reaction mixture was an orange homogeneous solution. It was hydrolyzed with saturated aqueous NH_4Cl, washed with $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. A yellowish solid was obtained: NMR (C_6D_6) δ 7.1 (s). Minor signals at ca. δ 1 were detected. No vinylic protons were present.

E. **Reduction of *p*-Benzoquinone with Ni(acac)$_2$–Dibah.** Nickel bis(acetylacetonate) (0.07 g, 0.27 mmol) was dissolved in 10 mL of ether and cooled to −78 °C. It was reduced with an equimolar amount of Dibah (0.36 mL, 0.75 M) and stirred until the solution color was dark brown. *p*-Benzoquinone (0.114 g, 1.1 mmol) in 25 mL of THF was added via cannula. The dark reaction mixture was stirred at −78 °C for 45 min, after which it was hydrolyzed by pouring into dilute aqueous H_2SO_4. It was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated to give a brownish yellow solid. Analysis by GC/MS on column E gave a component with m/e 110, with a fragmentation pattern identical with that of standard *p*-hydroquinone. Other identifiable, high molecular weight components were present.

General Procedure for the Nickel-Catalyzed Cross-Coupling of an Alkenyl Group from 6 with Aryl Halides. The following general procedure illustrates the cross-coupling reaction catalyzed by nickel compounds. Ni(acac)$_2$ (0.0243 g, 0.10 mmol) was dissolved in 5 mL of THF [for studying the Negishi catalyst system, PPh_3 (4 equiv) was added at this point] and cooled to 0 °C. Dibah (0.13 mL, 0.75 M) was syringed in. Chlorobenzene (0.1163 g, 1.0 mmol), **6** (0.6 g, 1.77 mmol), and undecane, internal standard (0.0478 g), dissolved in 10 mL of THF, were added dropwise. The reaction was stirred at 0 °C for 3.5 h, then worked up in the usual manner and analyzed by VPC and GC/MS. Column F was used for iodobenzene experiments while column E was used for bromo- and chlorobenzene because of separation problems. Spectral data for **17** are as follows: ^1H NMR (CCl_4) δ 7.2 (m, 5), 6.28 (d, 1, J = 16 Hz), 6.10 (d, 1, J = 16 Hz), 1.1 (s, 9); mass spectrum m/e 160 (28.1), 145 (100), 117 (32.6), 91 (33.6), 77 (13.2). An identical procedure was performed using Ni(acac)$_2$–Dibah–4PPh$_3$ and Ni(acac)$_2$–**6**. In the former case PPh_3 was weighed into the flask together with Ni(acac)$_2$ prior to reduction with Dibah. In the latter case **6** and Ni(acac)$_2$ were weighed into the flask and dissolved in THF.

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Thermochemical Studies of Carbonyl Reactions. 2. Steric Effects in Acetal and Ketal Hydrolysis[1]

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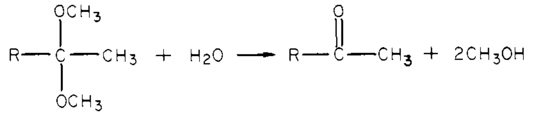
Abstract: A calorimetric determination of the enthalpies of hydrolysis of a series of alkyl-substituted dimethyl acetals is reported. These data are critically compared with the enthalpies of hydrolysis from an analogous set of aliphatic dimethyl ketals derived from 2-alkanones. The acetals exhibit a significantly attenuated range in their enthalpies of hydrolysis relative to that for ketal hydrolysis. The free energies of acetal formation in solution were modeled by measurements of the corresponding free energies of hemiacetal formation from the aldehydes in neutral methanol. The observed free-energy differences are satisfactorily correlated with the Taft E_s steric substituent constant scale, but the corresponding acetal enthalpy data vary in a complex manner. The role of entropy in determining kinetic and equilibrium steric effects in a variety of other systems is discussed. Preliminary molecular mechanics calculations on these systems indicate the importance of bond angle bending in evaluating the torsional potential at a carbonyl group. Many of the compounds were found to possess several conformations having comparable energies.

Steric effects on rates and equilibria are commonly observed in reactions that involve the interconversion of a trigonal carbon and a more crowded tetrahedral carbon. Examples of this type of reaction include the hydrolysis of aliphatic esters,[3] addition reactions of carbonyl compounds and olefins,[4] oxidations of secondary alcohols,[5] and the solvolysis of tertiary alkyl halides.[6] For many of these reactions the rate or equilibrium differences among the members of a reaction series correlated with the relative size of the substituent groups attached to the reaction center.[3,7]

We have obtained information on the enthalpy component of steric effects associated with trigonal–tetrahedral transformations by an examination of the enthalpies of hydrolysis of dimethyl ketals derived from alkyl methyl ketones[1] (eq 1). Through a combi-



$$R-C(OCH_3)_2-CH_3 + H_2O \longrightarrow R-C(=O)-CH_3 + 2CH_3OH \qquad (1)$$

nation of calorimetric results with equilibrium constant mea-

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