Synthetic Explorations Involving Nickel Acylate Complexes and Electrophilic Alkenes†

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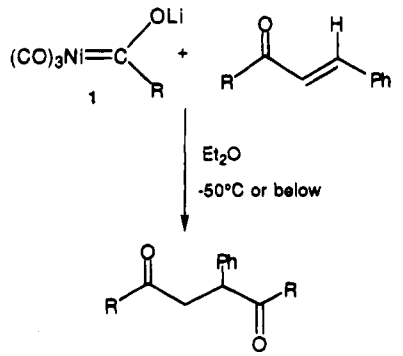
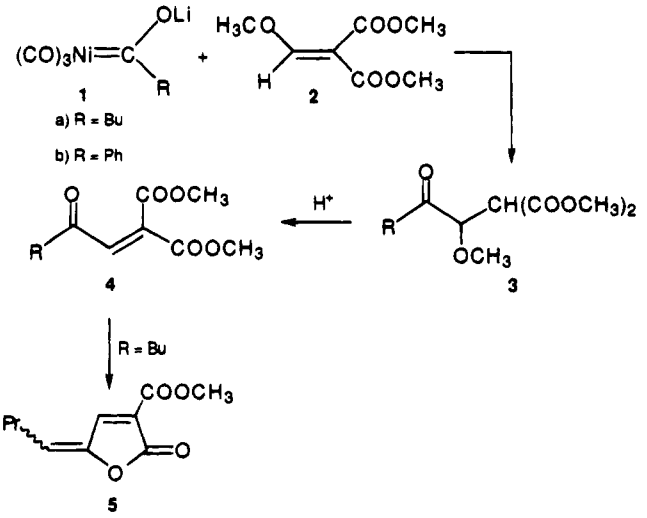
It first was shown about 25 years ago that an alkylnickel acylate complex, such as **1**, in Et_2O at −50 °C or below, reacts with an α,β-unsaturated ketone to generate a 1,4-diketone.[1]



The use of these alkylnickel acylate complexes, and the corresponding alkoxy and amido acylate complexes, for the conjugate (Michael) addition to α,β-unsaturated ketones and esters has figured in several investigations.[1-3] Recently, we have been studying the mechanism(s) of reactivity of these nickelacylate complexes[4] and, by doing so, extending their synthetic scope.[5] In this note, we show that nickel acylate complexes react with other types of electrophilic double bonds and that these reactions provide a ready route to organic carbonyl derivatives such as butenolides, nitroketones, diketones, α,β-unsaturated esters, and α,β-unsaturated ketones, many of which are useful precursors to substrates required for our radical cyclization reactions.[6]

Before we begin, one point that must be mentioned is that we have shown spectroscopically that the structure of the acylate complex in Et_2O at −50 °C or below is **1**; however, this complex dimerizes when the temperature is raised to about −20 °C.[7] In contrast, the acylate complex in THF is stable upon warming to room temperature.[4] Thus, all the chemistry we will discuss in this note has been performed in THF due to the much wider temperature range it affords.

Functionalized Unsaturated Ketones. As mentioned above, there are examples in the literature of the reaction between a nickel acylate complex and an α,β-unsaturated ketone or ester to generate a 1,4-dicarbonyl compound. However, to the best of our knowledge, there are no examples of a reaction between a nickel acylate complex and an α,β-unsaturated ketone or ester containing another functional group which can be used as a handle for chemistry subsequent to an initial conjugate addition.[1-3] To examine this possibility, methoxy malonate derivative **2** was treated with acylate complex **1a**, and the expected conjugate-addition product, compound **3a**, results in 89% yield (yields are for isolated materials). Reaction of **3a** with sulfuric acid not only gives elimination (to putative intermediate **4a**) but also cyclization to the butenolide derivative **5a** in 95% yield. Thus, nickel acylate chemistry represents a very efficient method for the synthesis of the butenolide ring system from readily available starting materials. Butenolides, such as **5a**, are key synthetic building blocks for several approaches to lignan natural products,[8] as Diels–Alder dienophiles, and as Michael acceptors.



Similarly, treatment of malonate derivative **2** with acylate complex **1b** generates compound **3b** in 79% yield. Reaction of **3b** with sulfuric acid also gives elimination of methanol, but here the product did not cyclize and, thus, compound **4b** is isolated in 90% yield.

Conjugate Addition to Unsaturated Nitro Compounds. In an attempt to determine the ability of nickel acylate complexes to undergo Michael additions to compounds other than α,β-unsaturated ketones and esters,

† The authors would like to dedicate this paper to the memory of Mr. Chester Rosansky, a former student, colleague, and friend.

(1) (a) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233, 4926. (b) Hegedus, L. S. Ph.D. Thesis, Harvard University, Cambridge, MA, 1970.

(2) (a) Ryang, M.; Myeong, S. K.; Sawa, Y.; Tsutsumi, S. *J. Organomet. Chem.* **1966**, *5*, 305. (b) Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183. (c) Myeong, S. K.; Sawa, Y.; Ryang, M.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 330. (d) Sawa, Y.; Hashimoto, I.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1968**, *33*, 2159. (e) Fukuoka, S.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1968**, *33*, 2973; **1970**, *35*, 3184; **1971**, *36*, 2721.

(3) Also see: (a) Hegedus, L. S.; Tamura, R. *Organometallics* **1982**, *1*, 1188. (b) Semmelhack, M. F.; Brickner, S. J. *J. Org. Chem.* **1981**, *46*, 1723. (c) Semmelhack, M. F.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. *J. Org. Chem.* **1985**, *50*, 5566. (d) Semmelhack, M. F.; Keller, L.; Sato, T.; Spiess, E. *J. Org. Chem.* **1982**, *47*, 4382.

(4) (a) Simunic, J. L.; Pinhas, A. R. *Organometallics* **1987**, *6*, 1358. (b) Simunic, J. L.; Pinhas, A. R. *Inorg. Chem.* **1989**, *28*, 2400. (c) Pinhas, A. R.; Hershberger, J. W. *Organometallics* **1990**, *9*, 2840.

(5) (a) Chamchaang, W.; Pinhas, A. R. *J. Chem. Soc., Chem. Commun.* **1988**, 710. (b) Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2943. (c) Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2531.

(6) (a) Belletire, J. L.; Mahmoodi, N. O. *Tetrahedron Lett.* **1989**, *30*, 4363. (b) Belletire, J. L.; Mahmoodi, N. O. *J. Nat. Prod.* **1992**, *55*, 194. (c) Fremont, S. L.; Belletire, J. L.; Ho, D. M. *Tetrahedron Lett.* **1991**, *32*, 2335.

(7) LaDuca, M. J. T., Simunic, J. L.; Hershberger, J. W.; Pinhas, A. R. *Inorg. Chim. Acta* **1994**, *222*, 165.

(8) (a) Tomioka, K.; Koga, K. *Heterocycles* **1979**, *12*, 1523. (b) Tomioka, K.; Ishiguro, T.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 652. (c) Tomioka, K.; Ishiguro, T.; Koga, K. *Chem. Pharm. Bull. Jpn.* **1985**, *33*, 4333.

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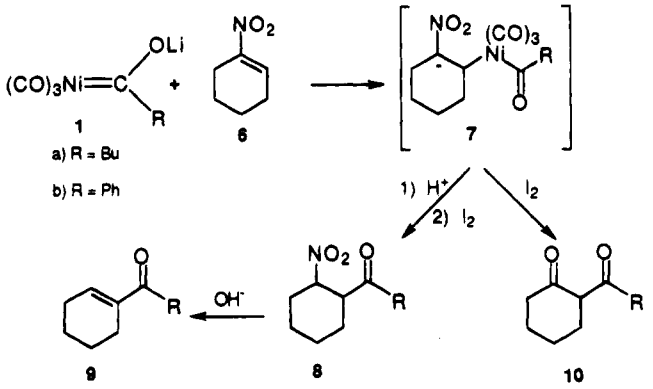
we treated pentanoyl acylate complex **1a** with 1-nitrocyclohexene (**6**). When this reaction is worked up first with NH_4Cl (to quench the negative charge) and then with I_2 (to remove the nickel from the product), butyl 2-nitrocyclohexyl ketone (**8a**) is generated in 59% yield. When compound **8a** (either crude or purified) is treated with a base, butyl cyclohexenyl ketone **9a** is produced in 30% yield. When the Michael addition reaction is treated directly with I_2, followed by our usual workup with sodium bisulfite and water, 1,3-diketone **10a** is the resulting product (47% yield). Thus, taken in conjunction with previous research,[1-3] nickel acylate complexes can be used to generate a 1,2-diketone, a 1,3-diketone, a 1,4-diketone, or an α,β-unsaturated ketone.



In a similar fashion, benzoyl acylate complex **1b** upon reaction with **6** generates the somewhat unstable 2-nitrocyclohexyl phenyl ketone (**8b**), which, without purification, can be treated with base and converted to ketone **9b**, but only in 15% yield for the two steps. As above, when the intermediate from the Michael addition (**7b**) is treated directly with I_2, 1,3-diketone **10b** is formed in 35% yield.

At this time, a few questions need to be answered and we addressed them using butyl complex **1a**. The first question is what is the intermediate from the initial Michael addition that generates nitro compound **8** and ketone **10**? In particular, does this compound contain nickel? It is known that an anionic nitro compound, upon oxidation, generates an aldehyde or ketone,[9] and we have found that compound **8** upon treatment with potassium hydride, to generate the anion, followed by I_2, as the oxidant, gives compound **10**. However, on the basis of infrared spectral data, in particular the presence of peaks in the region associate with terminal carbonyls of a five-coordinate nickel(II) species (1995 and 1949 cm^{-1}),[4] we have proposed that the intermediate still contains the nickel and, thus, has structure **7a**.

Second, to help determine the exact role of the I_2, which can act as either an inner sphere or as an outer sphere oxidizing agent, in the conversion of **7a** to **10a**, the reaction between acylate complex **1a** and nitrocyclohexene **6** was oxidized instead with ferrocenium ($Cp_2Fe^+BF_4^-$), which can act only as an outer sphere oxidizing agent.[4c] Here the oxidation reaction generates compound **8** and only small amounts of 1,3-diketone **10** were obtained. This result suggests that the I_2 is acting as an inner sphere oxidizing agent and, therefore, is adding to intermediate **7a** rather than just removing an electron from it. The resulting iodo–nitro compound then must rearrange and eliminate to form the diketone.

Conclusion. We have shown that a nickel acylate complex undergoes facile reactions with a variety of electrophilic double bonds to generate, in modest to good yields, highly-functionalized organic products.

Experimental Section

General. All reactions were carried out using glassware dried in a 110 °C oven and cooled under an argon atmosphere or in a desiccator. All reactions were run under an inert atmosphere. Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl. Nickel tetracarbonyl was transferred from a 1 lb lecture bottle into a 10 mL side-arm flask, maintaining a strong argon flow, and stored under argon until used. Transfers were made via syringe, and excess $Ni(CO)_4$ was quenched in an iodine/CCl_4 bath. (Caution: $Ni(CO)_4$ is very toxic and flammable when exposed to air. All work should be conducted in a well-ventilated hood, maintaining an argon atmosphere during all transfers and using nonflammable solvents in the iodine bath to reduce the probability of fire.)

Instrumentation. Gas chromatographic analyses were done using a flash vaporization injector at 225 °C, a flame ionization detector at 270 °C, and a 10 ft × 1/8 in. 5% SP-2100 on 100/120 Supelcoport column. Temperature programming was used: 50 °C hold for 2 min, increase at 10 °C per minute to 250 °C, then increase at 30 °C per minute to 300 °C, and hold for 6.5 min. All infrared spectra were recorded on an FT-IR spectrophotometer using KBr or CaF_2 cells. All NMR spectra were recorded on a 250 MHz spectrometer. All low-resolution mass spectra were obtained on a GCMS using a 0.25 mm × 15 m fused silica capillary SPB-1 column and temperature programming. High-resolution mass spectra were done by direct inlet.

Nickel Acylate Complex 1. This was done in a similar manner to the published procedure.[4] To a 3-neck round-bottom flask, under an inert atmosphere and equipped with a glass stopper, a rubber septum, a stir bar, and a gas inlet adapter, was added between 25 and 35 mL of degassed THF. The solvent was cooled to −78 °C, and 0.60 mL (5.0 mmol) of nickel tetracarbonyl was added. To this was added 3.1 mL of 1.6 M butyllithium (5.0 mmol) or 2.8 mL of 1.8 M phenyllithium over a 15 min period. (It has been found that near the end of the addition there is a significant darkening of the color of the reaction mixture. Cleaner reactions result when the addition is stopped at this point.) The reaction was kept at −78 °C for an additional 15 min and then allowed to warm to room temperature for 1 h.

Dimethyl (Methoxymethylene)malonate (2). The synthesis of this compound was adapted from the *Organic Syntheses* preparation of ethyl (ethoxymethylene)malonate.[10] Due to the greater volatility of the reagents used to make the methyl analog, the temperature of the final 2 h heating period was reduced from the published 145–155 °C to 120 °C. The product was purified by Kugelrohr distillation. The fraction collected between 80 and 110 °C (ca. 2 Torr) contained 3.4 g (20 mmol, 20% yield based on dimethylmalonate) of **2**. GC t_R: 13.5 min. ^1H NMR ($CDCl_3$) δ: 7.60 (s, 1H), 4.99 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 165.7 (CH), 165.2 (C), 164.2 (C), 105.7 (C), 63.4 (CH_3), 52.1 (CH_3), 52.0 (CH_3). IR (CCl_4): 2989 (m), 2954 (m), 2848 (m), 1731 (bd vs), 1637 (vs) cm^{-1}. MS (EI) *m/e* (rel intensity): 175 (1), 174 (19), 145 (8), 143 (67), 75 (100), 69 (12). HRMS: exptl 174.0507, calcd for $C_7H_{10}O_5$ 174.0528.

Methyl 2-Carbomethoxy-3-methoxy-4-oxooctanoate (3a). To a 3-neck flask, equipped with a glass stopper, a gas inlet adapter, and a rubber septum, under an inert atmosphere, was added 0.87 g (5.0 mmol) of malonate derivative **2** dissolved in 20 mL of degassed THF. The solution was cooled to 0 °C. To this, over a 15 min period, was added 5.0 mmol of pentanoylnickel acylate complex **1a** in 40 mL THF. The reaction mixture was allowed to stir an additional 15 min at 0 °C. To this was added 10 mL of a degassed, saturated NH_4Cl solution.

(9) See, for example: (a) Noland, W. E. *Chem. Rev.* **1955**, *55*, 137. (b) Shechter, H; Williams, F. T. *J. Org. Chem.* **1962**, *27*, 3699. (c) Kornblum, N.; Erickson, A. S.; Kelly, W. J.; Henggeler, B. *J. Org. Chem.* **1982**, *47*, 4534.

(10) Parham, W. E.; Reed, L. J. *Organic Syntheses*; J. Wiley and Sons: New York, 1955; Collect. Vol. 3, p 395.

The reaction mixture was allowed to warm to room temperature and, after 30 min, was poured directly onto 1.4 g (5.5 mmol) of solid I_2 and allowed to react for 15 min. A 10% $NaHSO_3$ solution was added to remove excess I_2, and the entire mixture was extracted with 75 mL of Et_2O. The organic layer was washed with additional bisulfite until the water layer was clear. The organic layer was then washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The solvent was removed under vacuum, leaving 1.16 g (4.33 mmol, 84% yield) of **3a**, a slightly yellow clear oil which is essentially pure. GC t_R: 16.1 min. ^1H NMR ($CDCl_3$) δ: 4.23 (d, J = 7.1 Hz, 1H), 3.97 (d, J = 7.1 Hz, 1H), [3.76 (s), 3.73 (s), 6H], 3.50 (s, 3H), 2.82–2.50 (m, 2H), 1.57 (quintet, J = 7.3 Hz, 2H), 1.34 (sextet, J = 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 208.9 (C), 166.9 (C), 166.8 (C), 83.5 (CH), 59.2 (CH_3), 53.3 (CH), 52.3 (CH_3), 38.5 (CH_2), 24.7 (CH_2), 21.8 (CH_2), 13.5 (CH_3). IR (neat oil): 2952 (s), 2936 (s), 2873 (m), 2836 (m), 1755 (vs sh), 1740 (vs), 1719 (vs sh) cm^{-1}. MS (EI) m/e (rel intensity): 261 (5), 260 (13), 245 (30), 197 (47), 177 (37), 175 (100), 131 (40), 117 (37), 113 (32), 85 (82), 75 (88). HRMS: exptl 260.1272, calcd for $C_{12}H_{20}O_6$ 260.1260.

5-Butylidene-3-carbomethoxy-2(5*H*)-furanone (5a). Under an inert atmosphere, to a mixture of 2 mL of benzene and 1 drop of concd H_2SO_4 (from a Pasteur pipette) was added 0.265 g (1.02 mmol) of the methoxy malonate derivative **3a** dissolved in 2 mL of benzene. This mixture was heated to reflux in an oil bath for 4 h and then was allowed to stir overnight at room temperature. A small amount of solid, anhydrous K_2CO_3 was added to neutralize the H_2SO_4, and after filtration, the benzene was removed under reduced pressure. The resulting oil was dissolved in EtOAc and filtered through a short plug of silica (<200 mesh), using pure EtOAc as the solvent, to give 0.190 g (0.97 mmol, 95% yield) of **5a**. GC t_R: 17.8 min. ^1H NMR ($CDCl_3$) δ: 7.98 (s, 1H), 5.67 (t, J = 8.1 Hz, 1H), 3.90 (s, 3H), 2.45 (dt, J = 8.1, 7.4 Hz, 2H), 1.40 (sextet, J = 7.4 Hz, 2H), 0.97 (t, J = 7.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 164.9 (C), 161.0 (C), 148.7 (CH), 147.4 (C), 124.9 (CH), 121.7 (C), 52.5 (CH_3), 29.1 (CH_2), 22.0 (CH_2), 13.8 (CH_3). IR (neat oil): 3096 (m), 2955 (m), 2926 (m), 2870 (m), 1796 (vs), 1729 (s), 1663 (m) cm^{-1}. MS (EI) m/e (rel intensity): 197 (8), 196 (77), 167 (48), 164 (39), 140 (100). HRMS: exptl 196.0725, calcd for $C_{10}H_{12}O_4$ 196.0736.

Methyl 2-Carbomethoxy-3-methoxy-4-oxo-4-phenylbutanoate (3b). A procedure similar to the one used for the synthesis of **3a** was used for **3b**. After the solvent was removed under reduced pressure, a clear yellow oil was obtained. This oil was dissolved in 1 mL of a 1:99 Et_2O:petroleum ether mixture and was loaded on a column containing 32 g of silica gel. The column was eluted first with 600 mL of a 1:99 Et_2O:pet. ether mixture and then with 900 mL of a 1:99 EtOAc:petroleum ether mixture to give 0.73 g (2.6 mmol, 78% yield) of **3b**. GC t_R: 20.0 min. ^1H NMR ($CDCl_3$) δ: 8.07 (d, J = 7.8 Hz, 2H), 7.61 (m, 1H), 7.50 (t, J = 7.7 Hz, 2H), 5.38 (d, J = 9.8 Hz, 1H), 4.27 (d, J = 9.8 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 3.32 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 196.5 (C), 167.6(C), 167.0 (C), 135.7 (C), 133.8 (CH), 128.9 (CH), 128.8 (CH), 78.6 (CH), 57.1 (CH_3), 52.9 (CH), 52.7 (CH_3). IR (neat oil): 3006 (m), 2948 (m), 2834 (m), 1753 (vs sh), 1735 (vs), 1689 (vs) cm^{-1}. MS (EI) m/e (rel intensity): 249 (4), 248 (16), 217 (22), 105 (100), 84 (22), 77(50), 75 (65). HRMS: exptl 280.0908, calcd for $C_{14}H_{16}O_6$ 280.0947.

Methyl 2-Carbomethoxy-4-oxo-4-phenyl-2-butenoate (4b). To a mixture of 2 mL of dry benzene and 1 drop of concd H_2SO_4 from a Pasteur pipette was added 0.118 g (0.42 mmol) of methoxy keto diester **3b** dissolved in 5 mL of dry benzene. Under an inert atmosphere, the mixture was heated to reflux in an oil bath for 4 h and then was allowed to stir overnight. A small amount of anhydrous K_2CO_3 was added to neutralize the H_2SO_4. The solution was then filtered and the benzene removed under vacuum. The residue was dissolved in EtOAc and filtered through a short plug of silica (<200 mesh) using pure EtOAc to give 0.094 g (0.38 mmol, 90% yield) of **4b**. GC t_R: 19.9 min. ^1H NMR ($CDCl_3$) δSPCLN 7.97 (d, J = 7.6 Hz, 2H), 7.90 (s, 1H), 7.67–7.61 (m, 1H), 7.54–7.49 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 188.9 (C), 165.2 (C), 163.3 (C), 136.1 (C), 136.1 (C), 135.7 (CH), 134.4 (CH), 129.1 (CH), 129.0 (CH), 53.4 (CH_3), 53.0 (CH_3). IR (neat oil): 3060 (w), 3030 (w), 3007 (w), 2955 (m), 1741 (vs), 1738 (vs), 1671 (vs), 1624 (m) cm^{-1}. MS (EI) m/e (rel intensity): 249 (3), 248 (21), 105 (100), 77 (51). HRMS: exptl 248.0685, calcd for $C_{13}H_{12}O_5$ 248.0697.

Butyl 2-Nitrocyclohexyl Ketone (8a). To a solution of 5.0 mmol of pentanoylnickel acylate complex **1a** dissolved in 35 mL of THF and cooled to −20 °C was added 0.57 mL (5.0 mmol) of neat 1-nitrocyclohexene over a period of 1 min. The reaction was kept at −20 °C for an additional 15 min, and then the cold bath was removed and the reaction mixture was allowed to stir an additional 3 h at room temperature. The carbonyl region of the IR spectrum of this reaction mixture consisted of the following peaks: 1995 (vs), 1949 (s), 1821 (s), 1797 (s), and 1712 (w) cm^{-1}. To this reaction mixture was added 15 mL of a degassed, saturated NH_4Cl solution. After 2 h, the mixture was poured directly onto 1.9 g (7.5 mmol) of solid I_2. A 10% $NaHSO_3$ solution was added to remove excess I_2, and the entire mixture was extracted with 75 mL of Et_2O. The organic layer was washed with additional bisulfite until the water layer was clear. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The solvent was removed under vacuum. The resulting oil was chromatographed on 25 g of silica gel, eluting first with 300 mL of 1:99 EtOAc:petroleum ether, followed by 300 mL 1.5:98.5 EtOAc: petroleum ether, and finally 200 mL of 3:97 EtOAc:petroleum ether to give 0.63 g (3.0 mmol, 59% yield) of **8a**. GC t_R: 18.0 min. ^1H NMR ($CDCl_3$) δ: 4.73 (dt, J = 11.3, 4.7 Hz, 1H), 3.13 (dt, J = 11.4, 3.1 Hz, 1H), 2.58–2.48 (m, 3H), 2.13–2.08 (m, 1H), 1.96–1.92 (m, 1H), 1.85–1.82 (m, 1H), 1.71–1.65 (m, 1H), 1.62-1.51 (m, 2H), 1.14–1.17 (m, 5H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 210.5 (C), 84.6 (CH), 52.4 (CH), 41.2 (CH_2), 31.6 (CH_2), 28.1 (CH_2), 25.6 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 22.4 (CH_2), 14.0 (CH_3). IR (CCl_4): 2934 (s), 2935 (s), 2867 (m), 1718 (s) cm^{-1}. MS (EI) m/e (rel intensity): 167 (5), 166 (23), 124 (47), 109 (100), 85 (51), 81 (46). MS (CI) m/e (rel intensity): 214 (10), 167 (100), 109 (8), 85 (23). HRMS: exptl 166.1369, calcd for $C_{11}H_{18}O$ 166.1358.

Butyl 1-Cyclohexenyl Ketone (9a). The previous procedure for **8a** was repeated. After the solvent was removed under vacuum, the resulting oil was redissolved in 30 mL of THF and mixed with 10 mL of 0.5 M NaOH solution. This mixture was allowed to react at room temperature overnight. The solution was neutralized with dilute HCl and extracted with 75 mL of Et_2O. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The solvent was removed under vacuum. The resulting oil was chromatographed on a silica gel (16 g) column, eluting first with 200 mL of 0.75:99.25 EtOAc:petroleum ether followed by 250 mL of 1:99 EtOAc:petroleum ether to give 0.25 g (1.5 mmol, 30% yield) of **9a**. GC t_R: 14.5 min. ^1H NMR ($CDCl_3$) δ: 6.89 (br s, 1H), 2.61 (t, J = 7.6 Hz, 2H), 2.3–2.29 (m, 4H), 1.68–1.52 (m, 6H), 1.33 (sextet, J = 7.4 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 201.7 (C), 139.4 (CH), 139.3 (C), 36.7 (CH_2), 27.0 (CH_2), 26.1 (CH_2), 23.2 (CH_2), 22.6 (CH_2), 22.0 (CH_2), 21.6 (CH_2), 14.0 (CH_3). IR (CCl_4): 2957 (s), 2934 (vs), 2863 (m), 1662 (vs), 1637 (m) cm^{-1}. MS (EI) m/e (rel intensity): 167 (1), 166 (10), 124 (33), 109 (100), 81 (96), 79 (43). HRMS: exptl 166.1334, calcd for $C_{11}H_{18}O$ 166.1358.

Butyl 2-Oxocyclohexyl Ketone (10a). The procedure for **8a** was repeated except, after reacting 3 h at room temperature, the mixture was poured directly onto 2.50 g (10.0 mmol) of solid I_2. A 10% $NaHSO_3$ solution was added to remove excess I_2, and the entire mixture was extracted with 75 mL of Et_2O. The organic layer was washed with additional bisulfite until the water layer was clear. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The solvent was removed under vacuum. A sample was separated on 25 g of silica gel, eluting first with 200 mL of 1:99 EtOAc:petroleum ether, followed by 400 mL of 2:98 EtOAc: petroleum ether, to give 0.43 g (2.4 mmol, 47% yield based on 1-nitrocyclohexene) of **10a**. GC t_R: 16.6 min. ^1H NMR ($CDCl_3$) δ: 16.05 (s, 1H, D_2O exchangeable), 2.41 (t, J = 7.4 Hz, 2H), 2.36–2.27 (m, 4H), 1.74–1.65 (m, 4H), 1.59 (quintet, J = 7.7 Hz, 2H), 1.36 (sextet, J = 7.3 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 201.8 (C), 181.8 (C), 106.8 (C), 36.8 (CH_2), 31.2 (CH_2), 26.5 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 22.6 (CH_2), 21.8 (CH_2), 14.0 (CH_3). IR (CCl_4): 2957 (vs), 2936 (vs), 2869 (s), 1711 (w), 1618 (vs), 1588 (vs) cm^{-1}. MS (EI) m/e (rel intensity): 183 (1), 182 (13), 140 (19), 126 (7), 125 (100). HRMS: exptl 182.1330, calcd for $C_{11}H_{18}O_2$ 182.1307.

1-Cyclohexenyl Phenyl Ketone (9b). The procedure for **9a** was repeated with the only changes being the use of phenyl

acylate **1b** in place of **1a**, and the solution was allowed to react for 2 days at room temperature following addition of NaOH. The solvent was removed under reduced pressure, and the resulting oil was loaded on a column with 20 g of silica gel, eluting first with 300 mL of 0.75:99.25 EtOAc:petroleum ether, followed by 250 mL of 1:99 EtOAc:petroleum ether, to give 0.14 g (0.75 mmol, 15% yield) of **9b**. GC t_R: 18.0 min. ^{1}H NMR ($CDCl_3$) δ: 7.64–7.60 (m, 2H), 7.54–7.37 (m, 3H), 6.58 (dd, J = 6.0, 2.8 Hz, 1H), 2.45–2.38 (m, 2H), 2.30–2.23 (m, 2H), 1.79–1.64 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 198.2 (C), 144.1 (CH), 138.7 (C), 131.2 (CH), 129.8 (C), 129.0 (CH), 127.9 (CH), 26.1 (CH_2), 23.9 (CH_2), 22.0 (CH_2), 21.6 (CH_2). IR (CCl_4): 3088 (m), 3063 (m), 3031 (m), 2933 (s), 2859 (s), 1686 (m sh), 1673 (s sh), 1650 (vs), 1634 (s sh), 1599 (s) cm^{-1}. MS (EI) m/e (rel intensity): 187 (13), 186 (89), 185 (49), 157 (18), 105 (100). HRMS: exptl 186.1044, calcd for $C_{13}H_{14}O$ 186.1045.

2-Oxocyclohexyl Phenyl Ketone (10b). The procedure for **8a** was repeated, except acylate complex **1b** was used, and after 3 h at room temperature, the reaction mixture was poured directly onto 1.5 g (5.9 mmol) of solid I_2. A 10% $NaHSO_3$ solution was added to remove excess I_2, and the entire mixture was extracted with 75 mL of Et_2O. The organic layer was washed with additional bisulfite until the water layer was clear. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The solvent was removed under vacuum. The resulting oil was separated on a 30 g silica gel column, eluting with 1:99 EtOAc:petroleum ether to give 0.354 g (1.75 mmol, 35% yield based on 1-nitrocyclohexene) of **10b**. GC t_R: 19.4 min. ^{1}H NMR ($CDCl_3$) δ: 7.90 (d, J = 7.9 Hz, 2H), 7.59–7.43 (m, 3H), 4.40 (t, J = 6.8 Hz, 1H), 2.64–2.44 (m, 2H), 2.39–2.27 (m, 1H), 2.17–1.88 (m, 4H), 1.79–1.68 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 208.7 (C), 197.7 (C), 136.6 (C), 133.3 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 58.9 (CH), 42.3 (CH_2), 30.1 (CH_2), 27.4 (CH_2), 23.5 (CH_2), 23.2 (CH_2). IR ($CDCl_3$): 3063 (w), 2947 (m), 2909 (sh), 2869 (m), 1712 (vs), 1677 (vs) cm^{-1}. MS (EI) m/e (rel intensity): 203 (7), 202 (51), 201 (40), 105 (100). HRMS: exptl 202.0997, calcd for $C_{13}H_{14}O_2$ 202.0994.

Reaction of 7a with Cp_2Fe^+ BF_4^-. To a solution of 3.0 mmol of pentanoyl nickel acylate complex dissolved in 35 mL of THF and cooled to −30 °C was added 0.34 mL (0.38 g, 3.0 mmol) of neat 1-nitrocyclohexene (**6**) over a period of 1 min. The reaction was kept an additional 15 min at −30 °C, at which point the cold bath was removed and the reaction mixture was allowed to stir an additional 1.5 h at room temperature. To this was added 0.82 g (3.0 mmol) of solid $Cp_2Fe^+BF_4^-$, and the solution was allowed to react for 3 h. The reaction was quenched with 10 mL of water and extracted with 75 mL of Et_2O. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with $MgSO_4$. The reaction mixture was injected into the GCMS. The ratio of **8a** to **10b** was determined to be 92%:8% from the integrated areas of the GC.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **3a**, **3b**, **4b**, **5a**, **8a**, **9a**, **9b**, **10a**, and **10b** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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